Enhancement of magnetic properties of PVDF by synthesize nano composite using NiZn ferrite.

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Abstract. The (XRD) patterns of the samples Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ in the form of powder were prepared using the ball milling technique for 41, 67 and 90 hours and were annealed at 1073, 1273 and 1373 K and (Poly vinylidine Fluoride) (PVDF) and composite samples of x% Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PVDF, (x%= 5, 10, 15, 20 and 25%) have been studied. The α phase decrease and β-phases increase by increasing the ferrite content suggesting less crystallinity producing an amorphous structure of PVDF at x=25% ferrite where as β PVDF nucleates in the composites The electric polarization increases by increasing NZF content. The transition from ferromagnetic (order state) to paramagnetic (disorder state) occurs at Curie temperature $T_c$ (600K). The DC resistivity is nearly constant from 153k to 286k for all composite samples and then decreases at high temperature. The behavior of dielectric constant and dielectric loss was measured in the temperature range from 200K to 700K. With the increase of magnetic content, the saturation magnetization ($M_s$) value of the composites also increases.

1. Introduction
The general chemical formula of spinel ferrites is MeFe$_2$O$_4$, [1], where Me represents a divalent metal ion with an ionic radius approximately between 0.6 and 1Å. In the case of simple ferrites, Me is one of the divalent ions of the transition elements such as Mn, Fe, Co, Ni, Cu and Zn. A combination of these ions is also possible. Furthermore, the symbol Me can represent a combination of ions which have an average valency of two: for example Li$^{1+}$ and Fe$^{3+}$ in lithium ferrite Li$_{0.5}$Fe$_{2.5}$O$_4$. The trivalent iron ions (ferric ions) in Me Fe2O4, can completely or partly be replaced by another trivalent ion such as Al$^{3+}$ or Cr$^{3+}$, giving rise to mixed crystals with aluminates and chromates. These compounds are also ferrimagnetic at room temperature if the non-magnetic ions are present in small concentrations. If the ferric ions are partly replaced by one of the tetravalent ions Ti$^{4+}$ or Ge$^{4+}$, the valency of an equal part of the ferric ions is lowered by one. A great variety in the chemical composition of oxides with spinel structure is possible [2]. At present, many polymers, such as PVDF, polyethylene, and polystyrene can be used as dielectrics in capacitors due to their large electric breakdown. PVDF represents one of the most important polymers because of its chemical stability, high elasticity modulus, and very high piezoelectric response compared with other polymers, which makes it useful in the fabrication of actuators and sensors. In addition, PVDF is the most selected material to be used as a dielectric, due to its high dielectric strength and permittivity, and low dissipation factor [3–5]. The aim of the present study is to obtain NZF in nanometre scale by ball milling and then make composite with PVDF to enhance the magnetic and electrical properties of PVDF.
2. Experimental Details.

2.1. Sample Preparation.

Fe$_2$O$_3$, ZnO and NiO powders with purity 99.9% where used as starting materials with molar ratio, one type of sample series Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ was synthesized from these powders by high energy ball milling. Raw materials of the ferrite samples Ni$_y$Zn$_{1-y}$Fe$_2$O$_4$ (where y= 0.5) has been taken in stoichiometric ratios. The powders were hand-ground in air using an agate mortar to obtain a homogeneous mixture of raw powders. Ball milling of powder mixture was conducted in a planetary ball mill to 41, 67 and 90 h using ball to powder mass ratio of (8: 18: 1). The crushed mass was milled and pressed as disks and toroids at 5000 kg/cm$^2$. Isothermal annealing of powders was carried out at 1073 K, 1273 K and 1373 K for 4h under air to eliminate then left to be cooled gradually with the rate 50 K/h, the milling induced crystal strain, defects and the oxide phases.

2.2. Sample Characterization.

X-ray studies were carried out by X-ray diffractometer at room temperature using a Philips model (PW-1729) using radiation source Cu-K$\alpha$ radiation ($\lambda$=1.5411Å). Infrared spectra (IR) of the investigated samples were recorded using the infrared spectrometer, (BRUKER FTIR spectrometer tensor 27) in the range 200–4000 cm$^{-1}$. The shape and morphology of the particles were analyzed using transmission electron microscope (TEM) model (JEOL- 100 SX). The magnetization M (emu/g) was measured at room temperature in a magnetizing field H using a vibrating sample magnetometer (VSM operating system v 1.6 control software Oxford OX8JTL England). An electrometer type 610 Keithly was used to measure the DC resistivity and RLC bridge type 815 B was used to measure dielectric constant and dielectric loss.

3. Results and Discussion

3.1. Structural Properties.

3.1.1. X-Ray Diffraction Analysis

The X-ray diffraction pattern (XRD) of the samples Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ for powder mixture milled for 41, 67 and 90 hours and annealed samples at 1073, 1273 and 1373K for the sample milled at 90 hour is shown in Fig. (1). The intensities of XRD peaks of oxides that appear are gradually decrease and sometimes totally disappear with increasing ball milling time.

In order to eliminate internal lattice strain and the other oxide phases and the crystal lattice defect, the samples were exposed to annealing process at 1037 K, 1273 K and 1373 K for 4 hours for the sample 90 hours milling. The intensity of peaks belongs to ferrite phase increased after annealing due to crystallite growth and reduction of internal strain.

The crystallite size after annealing was increased to 26 nm which lies in the range of nanomaterials. The dependence of crystallite size on calcination temperature and milling time are shown in Fig.2 (a,b) for the sample Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$. 
Figure 1. The XRD for Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$.

![Graph](image1)

(a) Crystallite size as function of (a) milling time and (b) calcination temperature and for the sample Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$.

Figure 2 (a, b). Crystallite size as function of (a) milling time and (b) calcination temperature and for the sample Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$.

The diffraction patterns of pure spinel phase of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and prepared by high energy ball milling technique for 90 hours and annealed at 1373 K for 4 hours are shown in Fig3. All peaks was matching the standard pattern of NiZnFe$_2$O$_4$ (JCDP) except for some peaks belong to ZnO at (2θ= 37 and 39°). Diffraction pattern of (PVDF) was shown in Fig 3. (b) and its nanocomposite with different percent of x% Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PVDF, (x=5-25%) prepared by high energy ball milling technique for 90 hours and annealed at 1373 K for 4 hours is shown in Fig. (4).
As seen there are three strong diffraction peaks at \((2\theta = 18.6\text{ and } 27^\circ)\) which are attributed to \(\alpha\)-phase of pure poly (Vinylidene fluoride) (PVDF) and at \((2\theta = 20.3^\circ)\) attributed to \(\beta\)-phase of PVDF. The spectra of the nanocomposite showed that incorporation of ferrite nanoparticle has a considerable effect on crystalline morphology structure of pure (PVDF) and by increasing ferrite percent, the (PVDF) diffraction peaks intensity decreases. The XRD diffractograms of the composite show broad peaks as a result of the presence of nanoparticles [6].

The crystallite sizes of the samples were estimated by broadening analysis of XRD peaks using Scherer's equation [7]:

\[
t = \frac{k \lambda}{\beta \cos \theta}, \quad (1)
\]

where \( k = 0.89 \) is constant, \( \theta \) is the diffraction angle, \( \beta \) is the full width at half maximum of the peak in radian, \( \lambda \) is the wave length of the X-ray for Cu-K\( \alpha \) radiation (\( \lambda = 1.541178\text{Å} \)).

![Figure 3(a, b). The XRD for (a) pure Ni\( \text{0.5Zn0.5Fe2O4} \) and (b) pure PVDF.](image)
3.1.2. Transmission Electron Microscopic (TEM) Analysis

Fig. (5) shows the TEM micrograph of pure PVDF and NZF/PVDF nanocomposites. It was found that the composite was made up of particles having distribution between 45.8 nm and 57.5 nm. Although XRD is useful tool for determining particle size it doesn't give information about size distribution. TEM can be used to give information about the shape of particles and its distribution. TEM micrograph of PVDF shows spherical particles with some agglomeration of nanoparticles.

Fig. (5): The TEM micrograph of pure PVDF and x% Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PVDF.
3.1.3. FT-IR Analysis

The room temperature IR spectra of the prepared ferrite Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ after ball milling 41 h, 67 h and 90 h and after calcination at 1073 K, 1273 K and 1373 K is shown in Fig.6 (a). The absorption band around 450 cm$^{-1}$ is assigned to the stretching vibration mode of Fe$^{3+}$-O$^2$ at octahedral site. The observed absorption band at around 785 cm$^{-1}$ belonging to the stretching vibration of Zn-O and that at 317 cm$^{-1}$ is attributed to stretching vibration of Ni-O. The absorption bands around 1100-1400 cm$^{-1}$ can be attributed to absorbed water and hydrocarbon impurities of the powder. $\nu_1$ and $\nu_2$ are assigned for the characteristics tetrahedral and octahedral absorption bands appeared in all spectra.

![Figure 6 (a, b). IR for (a) Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and (b) $x\%$Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PVDF nanocomposites.](image)

Figure 6 (b) shows the IR spectra for NZF/PVDF composite films in the range of (400-1500) cm$^{-1}$ respectively. Our FTIR spectra have absorption at 766, 1075, 1186, 1403 and 1432 cm$^{-1}$ indicating the presence of $\alpha$-phase PVDF. The absorption at 1403 represents the fingerprint of $\alpha$-phase. The molecular vibrations of $\gamma$-phase are very close to $\beta$-phase and it's difficult to separate $\gamma$-phase absorption. Only one absorption at 1234 cm$^{-1}$ is the evidence of $\gamma$-phase [8].

It was found from figure 6 (b) that the absorption intensity of $\alpha$-phase decreases by increasing NZF contents whereas the intensity of $\beta$-phase absorption still unchanged by increasing NZF content. The absorption at 602 and 471 cm$^{-1}$ indicating the stretching vibration modes of Fe$^{3+}$-O$^2$ at tetrahedral and octahedral sites respectively of ferrite phase. The absorption at 840 cm$^{-1}$ is assigned to a mixed mode of CH$_2$ and CF$_2$ asymmetric stretching vibration and the 511 cm$^{-1}$ absorption band is assigned to CF$_2$ bending mode [9].

The relative amount of $\beta$-phase $F(\beta)$ present in different samples were calculated by applying the equation [10,11,12,13]:

$$F(\beta) = \frac{I(\beta)}{I(\alpha) + I(\beta)}$$
where $A_\alpha$ and $A_\beta$ are the absorptions intensities at 745 and 839.4 cm$^{-1}$ which are corresponding to $\alpha$ and $\beta$ phase, $K_\alpha$ and $K_\beta$ are the absorption coefficient. The value of $K_\alpha$ is $6.1*10^4$ and $K_\beta$ is $7.7*10^4$ (cm$^2$/mole) [14]. The evaluation of $\alpha$ and $\beta$-phase content with ferrite concentration is observed in Fig. (7). The amount of $\beta$-phase increase and correspondingly the $\alpha$-phase decrease with increasing ferrite nanoparticle. These results are in agreement with the results of X-ray diffraction for our composite.

\[ F(\beta) = \frac{A_\beta}{(K_\beta/K_\alpha)A_\alpha + A_\beta}, \quad (2) \]

Figure 7. The relative amount of $\beta$-phase $F(\beta)$ as a function of $x\%$ Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PVDF.

3.2. Electrical Properties.

3.2.1. DC Electrical Resistivity.

The temperature dependence of DC electrical resistivity for both Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and $x\%$ Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PVDF samples is shown in figure 8 (a,b) in the temperature range from room temperature up to 833 K. The Curie temperature $T_C$ is found to equal 600 K for Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ in which the transition from ferrimagnetic to paramagnetic states occurs. The first region (I) in DC resistivity vs. $1000/T$ belongs to impurity phase which obeys the band theory conduction mechanism. The second region (II) is ferrimagnetic region which transform to paramagnetic region (III) at Curie temperature. The conduction mechanism in ferrite can be explained on the bases of hopping electrons between Fe$^{2+}$ and Fe$^{3+}$ at octahedral site. It was reported that Ni ions occupy octahedral site and Zn ions occupy tetrahedral site. When Ni replace Zn ion, the concentration of iron ions decreases on octahedral site.
The activation energy for ferromagnetic region \( E_f \) and for paramagnetic region \( E_p \) for ferrite sample is given in Table (1). The paramagnetic activation energy \( E_p \) has larger value than \( E_f \) which indicates influence of the magnetic state on the conduction behavior of the material. The low value of activation energy suggests that the conduction is due to thermally activated mobility. The room temperature resistivity of NZF/PVDF composites is measured by knowing the bulk resistance area and thickness of the film as a function of reciprocal temperature. It is found that the PVDF system shows higher resistivity than the corresponding NZF/PVDF composites. The decrease of crystallinity of the composite samples and the increasing of nanoferrite cause a decrease in resistivity. The decrease of resistivity with temperature is interpreted as being due to hopping mechanism which is feature of ferrite. The segmental motion of the polymer chain at higher temperature also causes the decrease of resistivity [15]. The higher the \( \beta \) phase content for the composite sample, the lower the resistivity of the sample [16].

For the samples under investigation, the conduction process can be attributed to the presence of two types of charge carriers \( n \)-type as electron transfer between \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \), and \( p \)-type as hole exchange between \( \text{Ni}^{2+} \) and \( \text{Ni}^{3+} \) at the octahedral sites. It has been concluded that the electron exchange between

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**Figure 8 (a, b).** The DC resistivity for (a) \( \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) and (b) \( x\%\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{PVDF} \) nanocomposites.
Fe$^{3+}$ and Fe$^{2+}$ results in the local displacement of charges, which is responsible for polarization in ferrites [17,18].

**Table (1):** The activation energy for ferromagnetic region $E_f$ and for paramagnetic region $E_p$ for ferrite sample.

| Sample           | $E_f$(eV) | $E_p$(eV) |
|------------------|-----------|-----------|
| Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ | 0.265     | 0.327     |

3.2.2. Dielectric Constant and Dielectric Loss
The variation of dielectric constant ($\varepsilon$) and dielectric loss (tan$\delta$) with temperature at constant frequency at 1kHz for Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ is shown in figure 9 (a, b). The dielectric constant gradually increases with temperature up to Curie temperature and then increase sharply above $T_C$. The temperature dependence of dielectric constant of ferrites attributed to four types of polarization, interfacial ($P_i$), dipolar ($P_d$), atomic ($P_a$) and electronic ($P_e$). At low frequencies all 4 types of polarization contribute. The rapid increase of $\varepsilon$ with temperature is mainly due to interfacial and dipolar polarization. The dielectric constant is nearly unchanged in the sample Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ in the temperature from (300-500K), and then sharply increase near 600 K. The sharp increase of $\varepsilon$ at higher temperature is due to the activation of conduction mechanism causing high dielectric constant and high dielectric loss (Tan$\delta$ >1).

The dielectric loss found to increase by increasing temperature and have the same behaviour of the dielectric constant. As the temperature increase the hopping frequency increases leading to the increase of the relaxation time and thus the increase of tan$\delta$. At higher temperature the conductivity and dielectric constant are thermally activated. The apparent increase of the dielectric constant at higher temperature is due to the thermal activation of conductivity causing high dielectric loss in this range. This is common behaviour found by different authors in the similar systems [19-23]. At low frequencies as in our case (1KHz) a rise in dielectric constant occur at high temperature due to the increase of space charge resulting from the increase of charge carrier concentration in paramagnetic region.

**Figure 9(a, b):** The variation of (a) dielectric constant and (b) dielectric loss with temperature at constant frequency for Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$.

Figure 10.(a, b) revealed that both dielectric constant ($\varepsilon$) and dielectric loss (tan $\delta$) for composite samples NZF/PVDF show a similar behaviour as pure PVDF. The dielectric constant and dielectric loss increase by increasing temperature and have a peak around glass transition temperature ($T_g$), this peak
shifts to higher temperature about 253 K for the sample 15% NZF content and 273K for other samples. The dielectric constant and dielectric loss are nearly independent on temperature up to 233K and then increase gradually around $T_g$ and then sharply increase at higher temperature. The figures also show the dielectric constant and dielectric loss decrease by increasing the frequency of the applied field.

The low temperature $\alpha$ relaxation assigned to the glass transition dynamics of pure polymer matrix is still present proving that the cooperative segmental motion with in the amorphous phase is also present in the composites [24]. The dynamic of $\alpha$ relaxation was analysed by Vogel- Fulcher- Tammann (VFT) relaxation formalism [24,25,26]:

$$\tau(T) = \tau_o e^{B/[K (T-T_o)]}$$

(3)

Where $\tau$ is the relaxation time, $B$ is the (VTF) energy, $\tau_o$ is the Vogel temperature at which the molecular motion in the material becomes infinitely slow and $T$ is the temperature [27]. The PVDF/NZF composite exhibit large dielectric constant compared with that of pure PVDF. The dielectric constant is three times larger than pure PVDF.
3.3. Magnetic Measurements.

3.3.1. Magnetic Permeability.

Figure 11 (a, b) represent the initial permeability $\mu_i$ of pure Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and x% Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanocomposite respectively. As shown in figure 11 (a) the initial permeability $\mu_i$ increases by increasing temperature and has a maximum at about 620K indicating the presence of single phase nanoferrite. After maximum it decreases sharply and reaches to minimum value due to the transition from ferrimagnetic to paramagnetic state, and the sample Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ give single spinel phase.

The thermal variation of the initial permeability $\mu_i$ was recorded to find the Curie temperature $T_C$ for both ferrite samples at 1 KHz in the temperature range from 300-700 K. These thermal spectra of permeability can be taken as a test of formation and homogeneity of ferrite samples. It's clearly shown that the curves has maximum permeability just below $T_C$ and sharply decrease behind $T_C$. The Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles have a sharp peak below $T_C$. This peak is called Hopkinson peak ($H_p$) in the vicinity of Curie temperature and confirmed the phase purity of the ferrite sample. The high of the peak depends on Ni content, the grain size variation and total magnetic anisotropy constant ($K_{eff}$).

The Curie temperature can be obtained from $\mu_i$-$T$ curve by extrapolating the linear part of the $\mu_i$-$T$ curve to the temperature axis. The obtained value of Curie temperature has the same value that obtained...
from DC conductivity and is given in Table (2). The behaviour of magnetic permeability versus temperature can be explained according to Globus model.

It is known that anisotropy constant usually decreased much faster with temperature than $M_s$ which leads to an initial increase to $\mu_i$. Near $T_C$ the sudden drop of $\mu_i$ is due to transformation from ferromagnetic to paramagnetic state. The rate of decrease in $\mu_i$ is given from the slope of linear part. It was found that this rate increases by increasing Ni content. The high rate of permeability with temperature for the Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ sample makes it very useful for the fabrication for devices of controlling temperature.

As shown in figure 11 (b) the permeability decreases sharply at temperature near the glass transition temperature ($T_g$) and reach its minimum value at the blocking temperature ($T_b$).
Figure 11 (a, b). Magnetic permeability for (a) Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and (b) x%Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PVD.

Table (2): The obtained value of Curie temperature which obtained from DC Conductivity and from $\mu_i$-T curve.

| Sample            | $T_C$ (K) from DC | $T_C$ (K) from $\mu_i$ |
|-------------------|-------------------|------------------------|
| Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ | 573              | 640                    |

3.3.2 Vibrating Sample Magnetometer (VSM).

The room temperature hysteresis measured for x%Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PVDF nanocomposites with different contents (x = 0, 5, 10, 15, 20, 25 and 100%) are shown in figure. (12).

Figure 12. VSM for x% Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PVDF.

From these hysteresis loops the experimental values of room temperature saturation magnetic moment $M_s$, the remnant magnetization $M_r$ and the coercive force $H_c$ were determined and given in table (3). The results show that $M_s$ continuously increase with increasing NZF content in the nanocomposite. As expected the magnetization of PVDF- ferrite composite are comparatively lower than the pure ferrite. This is mainly because Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles are embedded into a nonmagnetic polymer matrix.
With the increase of magnetic content, $M_s$ value of the composites also increase. These results suggest that ferrimagnetic behaviour observed in the composites arose from the magnetic nanoparticles. The value of $M_s$ for Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PVDF is equal to (65 (emu/g)) [30]. The lower values of saturation magnetization of the present nanocomposite is attributed to surface effects that are due to finite size of nanocrystallites, which in turn leads to a noncollinearity of magnetic moments on their surface [31]. The saturation magnetization $M_s$ decreases by increasing PVDF content. This suggests that the spontaneous magnetization of composite originate from the unbalanced antiparallel spins. The coercive field $H_c$ decrease by increasing the PVDF content.

| x%Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PVDF | $H_c$(G) | $M_s$(emu/g) | $M_r$(emu/g) |
|---|---|---|---|
| 5%Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ | 142.56 | 1.45 | 0.2 |
| 10%Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ | 44.62 | 1.75 | 65.65*10$^{-3}$ |
| 15%Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ | 157.53 | 2.17 | 0.33 |
| 20%Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ | 174.36 | 2.84 | 0.48 |
| 25%Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ | 148.69 | 7.24 | 0.99 |

4. Conclusion

Samples of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and composite films of x% Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/PVDF, (x%=5, 10, 15, 20 and 25%) were synthesized by high energy ball milling. The estimated particle sizes between (20 - 26) nm which is in agreement with those estimated from X-ray diffraction. The relative amount of β-phase F(β) increases while the α-phase decreases with increasing ferrite nanoparticle. The DC resistivity of the composite samples at room temperature reaches maximum at 5% NZF, above this ratio it begins to decrease. The dielectric constant of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ is sharply increased near 600 K due to the activation of conduction mechanism. The initial permeability $\mu_i$ increases by increasing temperature up to 620 K. Above this temperature, it decreases sharply and reaches to minimum value due to the transition from ferrimagnetic to paramagnetic state. The saturation magnetization and the coercive force decreases by increasing PVDF content in composites, which was appeared from VSM measurements.

References

[1] Smit J and Wijn H P J, 1961, "Les Ferrites", Dunod, Paris.
[2] Gorter E W 1954 Philips Research Reports 9 295..,
[3] Adireddy S, Puli V S, Lou T J, Elupula R, Sklare S, Riggs B C and Chrisey D B 2015, J. Sol-Gel Sci. Technol. 73 641.
[4] Wang Y, Zhou X, Chen Q, Chu B and Zhang Q 2010, IEEE Trans. Dielectr. Electr. Insul. 17 1036.
[5] Esterly D M 2002, Manufacturing of Poly (vinylidene fluoride) and Evaluation of its Mechanica Properties, M. Sc. Thesis Virginia Polytechnic Institute and State University.
[6] Bajaj B, Malhotra B D, and Choi S 2010 Thin Solid Films 519 (3) 1219.
[7] Rittidech A and Khotsongkram P 2006, American Journal of Applied Sciences 3 (3) 1760.
[8] Boccaccio T, Bottino A, Capanelli G and Piaggio P 2002, J. Membrane Sci. 210 (2) 315.
[9] Martins P, Lopes A C and Lanceros-Mendez S 2013, Progress in Polymer Science, accepted: http://dx.doi.org/10.1016/j.progpolymsci.2013.07.006.
[10] Gonçalves R, Martins P M, Caparrós C, Martins P, Benelmekki M , Lanceros-Mendez S, Lasheras A, Gutiérrez J, Barandiarán J M, and Botelho G 2013, Journal of Non-Crystalline Solids 361 93.
[11] Martins P, Costa C M, and Lanceros-Mendez S 2011, Appl. Phys. A 103 (1) 233.
[12] Silva M P, Botelho G, Rocha J G, and Lanceros-Mendez S 2010, Polymer Testing 29 613.
[13] Miranda D, Sencadas V, Sánches A, Pastoriza-Santos I, Liz-Marzán L, Ribelles J and Lanceros-Mendez S 2009, *J. Nanosci. Nanotechnol* 9 (5) 2910.
[14] Rajendran S, Sivakumar P, and Babu R S, 2006, *Bull. Mater. Sci.* 29 (7) 673.
[15] Martins P, Nunes J S, Hungerford G, Miranda D, Ferreira A, Sencadas V and Lanceros-Méndez S 2009, *Physics Letters* A 373 177.
[16] Iwauchi K 1971, Jpn. J. Appl. Phys. 10 (11) 1520.
[17] Rezulescu N and Rezulescu E 1974, *Physica Status Solidi (a)* 23 (2) 575.
[18] Qi X, Zhou J, Yue Z, Gui Z, Li L and Buddhudu S 2004, *Adv. Funct. Mater.* 14 (9), 920.
[19] Zhu W M and Ye Z G 2004, *Ceram. Int.* 30 (7), 1435.
[20] Van den Boomgaard J and Born R A J, 1978, *J. Mater. Sci.* 13 (7) 1538.
[21] Lupeiko T G, Lisnevskaya I V, Chkheidze M D, and Zvyagintsev B I 1995, *Inorg. Mater.* 31 1139.
[22] Yu Z and Ang C 2002, *J. Appl. Phys.* 91 (2) 794.
[23] Firmino Mendes S, Costa C M, Sencadas V, Serrado Nunes J, Costa P, Gregorio Jr R, and Lanceros Mendez S 2009, Applied Physics A, 96 (4) 899.
[24] Angell C A 1997, *Polym. J.* 38 (26) 6261.
[25] Li Y C, Tjong S C and Li R K Y 2011, *EXPRESS Polymer Letters* 5 (6) 526.
[26] Lanceros-Mendez S, Moreira M V, Mano J F, Schmidt V H and Bohannan G 2002, *Ferroelectrics* 273 (1) 15.
[27] Yang J, Park S B, Yoon H G, Huh Y M and Haam S 2006, *Int. J. Pharm.* 324 (2) 185.
[28] Cui L, Gu H, Xu H and D Shi 2006, *Mater. Lett.*, 60 (24) 2929.
[29] Jebeli Moeen Sh and Yousefi A A 2012, Proceedings of the ICNS4 p 1371.
[30] George M, John A M, Nair S S, Joy P A and Anantharaman M R 2006, *J.Magn. Magn. Mater.* 302 (1) 190.