Structural Investigations In Lithium Zinc Ferrites Containing Polypyrrole Composites

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Abstract:
Metallic oxides dispersed polymers constitutes a new class of polymer composites materials. Polypyrrole is a good conducting polymer with anti-electrostatic and anti-corrosion properties. In the present work the composites were prepared by mechanical mixing of polypyrrole and Li-Zn ferrite. The formation of composites and changes in the structural properties were investigated by characterizing the samples using XRD and EDAX techniques. Using Deby Scherrer equation, the crystalline sizes of particles were measured. EDAX study revealed that the lithium zinc ferrite oxide nanoparticles are evenly distributed throughout the polymer matrix.

Keywords:- Li-Zn ferrites; polypyrrole; polymer composites; EDAX, XRD.

1. Introduction

Due to their potential use in the fields of energy storage, optoelectronic devices, electrochromic materials, and organic photovoltaics, conducting polymers have attracted a great deal of attention in both academic and industrial research [1]. Researchers discovered that despite maintaining the processability and flexibility of normal polymers, conductive polymers exhibit magnetic, optical, and electrical properties similar to those of metals [2]. The method of doping with various compounds considerably improves the characteristics of polymers [3]. The functional materials like polymer-magnetic composites are obtained by simply mixing polymers with metal oxides [4]. Due to its outstanding chemical stability, high electromagnetic performance, and mechanical toughness, zinc ferrite ($ZnFe_2O_4$) has been the subject of much research. $ZnFe_2O_4$ nanoparticles have been combined with different polymeric materials in order to create distinctive and innovative conducting nanocomposites with electric and magnetic responses [5]. Low cost materials, such as pure and substituted lithium ferrites, are used in a wide range of technical applications [6–8]. Due to its high permeability (in the microwave frequency range) and high Curie temperature, lithium ferrite is used in a variety of high frequency electronic devices, including microwave circulators, isolators, phase shifters, and absorbers. In addition, Li-ferrite's strong electrical resistivity, mechanical toughness, and chemical stability make it appropriate for such applications [9,10]. The general formula for lithium ferrite, is $(A)[B_2]O_4$, and it has a spinel structure. Here, the tetrahedral site is represented by the parenthesis, and the octahedral site is represented by the square bracket [11].

In present work, we report the investigations of structural properties in $Li_{0.5-x/2}Zn_xFe_{2.5-x/2}O_4$ containing Polypyrrole composites.

2. Experimental

2.1 Materials

The pyrrole monomer, ammonium persulphate (APS), Li_2CO_3, ZnO and Fe_2O_3 chemicals and binding agent polyethylene glycol (PEG) were purchased from Sigma Aldrich of AR grade.

2.2 Synthesis of Polypyrrole

Polypyrrole (PPy) was synthesized by in-situ polymerization of monomer Pyrrole in the presence of oxidising agent (APS) Ammonium per sulphate. 0.3 M Pyrrole taken in a round bottomed glass flask was placed in an ice tray mounted on a magnetic stirrer. 0.6 M Ammonium per sulphate was added drop wise using a burette to the above 0.3 M pyrrole .The reaction was carried out for 6 h under continuous stirring maintaining temperature range 273 K–278 K. The resulting precipitate was removed by filtration by suction and rinsed with deionized water. The black polypyrrole powder thus obtained was then dried in a hot air oven and subsequently in a muffle furnace at a temperature of 373 K. The yield was 2.15 g, taken as 100 wt.% [12-15].

2.3 Synthesis of Lithium zinc ferrites

Lithium Zinc Ferrites were made using the combustion synthesis process, and their typical formula is $Li_{0.5-x/2}Zn_xFe_{2.5-x/2}O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0). Li_2CO_3, ZnO, and Fe_2O_3 (all of AR grade) were appropriately homogenized in a stoichiometric amount using an agate motor and pestle for an hour. PEG with a molecular weight of 6000 is added to the precursor in a 1:2 ratio, and the mixture is then ground for almost two hours to ensure sample consistency. The mixture is placed in a crucible, heated to up to 450^{o}C, and then allowed to cool to room temperature for about 5 hours. PEG, the binding agent, is first melted between 80 and 90^{o}C, and then the exothermic reaction is started at 450^{o}C. The resultant mixture is in powder form [16,18].

2.4 Synthesis of PPy/ Li-Zn ferrite composites

The samples were made using an equal weight mixture of PPy and Li-Zn ferrite ($Li_{0.5-x/2}Zn_xFe_{2.5-x/2}O_4$) that was manually homogenized in an acetone-containing medium. The pellets were made using an 80 MPa hydraulic press. The resulting pellets had a 10 mm diameter and varied 2 mm in thickness [18.19]. Further, multiple compositions of the composites (x = 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0) were used to label them, and the resulting composites were given the labels PLZF0, PLZF2, PLZF4, PLZF6, PLZF8, and PLZF10, respectively.

3. Characterization

The energy dispersive X-ray analysis with the composite PPy/ Li-Zn ferrite ratio is analyzed using (Make Bruker Germany) powder X-ray diffractometer instrument having a λ=1.5418x10^{-10} m for 2θ in the range 10^0 –80^0 .CuK-α source radiation is used for scanning the sample at the rate of 2^o /min. Using the EDAX genesis instrument, the nature of sample and formation crystalline structure is identified. [20]

4.Result and Discussion

4.1 EDAX Analysis

The Energy Dispersive analysis is used to find the composition of materials in the composites. In the composites the combination of each sample is formed weight percentage of polypyrrole 50 % and Li-Zn ferrite 50 % ($Li_{0.5-x/2}Zn_xFe_{2.5-x/2}O_4$) were observed from the EDAX. From the Fig.(1-d) show in the presence of Zn, Fe, Carbon and oxygen in the composites. The EDAX is not showing the presence of Li in the samples [16,22].

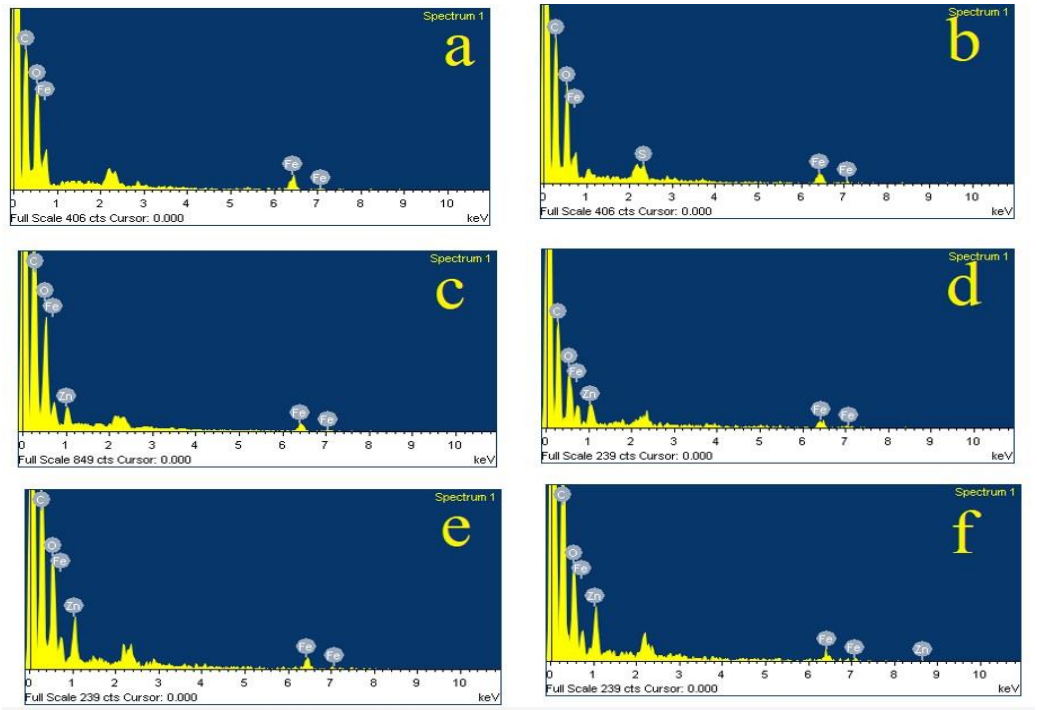

Fig.1(a-f) showing the EDAX images of (a)PLZF0 (b) PLZF2(c) PLZF4 (d) PLZF6 (e) PLZF8 and (f)PLZF10

4.2 X-Ray Diffraction analysis

The creation of the single-phase cubic spinel structure is depicted graphically by the x-ray diffraction pattern for various compositions in Figure 2. The features of the XRD pattern for the reflection planes from the range 2θ = 10°-80° are (220), (311), (400), (422), (511) and (440). The provided values are consistent with the face-centered cubic spinal structure(1-3) in the JCPDS file (Card no. 89-1009) [23]. In the composites, sharp peaks were observed showing the crystalline in nature of the composites.

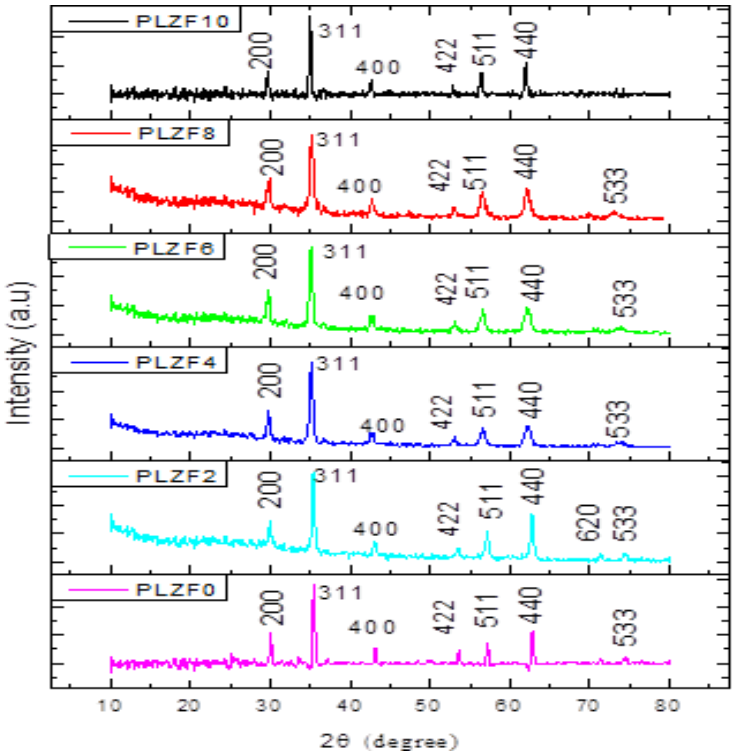

Fig.2 The X-ray diffraction pattern of PLZF0, PLZF2, PLZF4, PLZF6, PLZF8 and PLZF0

Crystallite Size

The average crystallite of the composites is analyzed using Debye-Scherrer's equation mentioned below was used to determine the average crystallite size of PZFL8 and PZFL10 [24].

$$d = \frac{k\lambda}{\beta cos\theta} \quad (1)$$

In this equation, K is constant at 0.89, D is the length of the axis parallel to the (hkl) plane, θ is the diffraction angle, β is the broadening of the diffraction line measured at half maximum intensity (radians), and λ = 1.5406, the wavelength of CuK. The composites that exhibit line broadening in the X-ray diffraction pattern provide proof that the material is crystalline. The average crystalline size of composites is estimated to be from 8.28 nm to 23.61 nm.

Inter-planar spacing(d)

The interplanar spacing for composites has been calculated using the Bragg's law [24,25],

$2d \sin\theta = n\lambda$ (2)

Where n is an integer, λ is the wavelength of the incident X-radiation, which is taken as 1.54 Å in the present study, d is the distance between atomic planes, 2θ is the diffraction angle in degree. The inter-planar spacing parameters for PLZF is shown in the Table 1.

Inter planar Spacing of PLZF8			Inter planar Spacing of PLZF10		
2θ in degree	**FWHM**	**d spacing (A°)**	**2θ in degree**	**FWHM**	**d spacing (A°)**
29.77337	0.54744	1.55123	29.64539	0.40411	1.55732
35.14707	0.58395	1.33807	35.00273	0.46345	1.34288
42.74542	0.54986	1.13489	42.57252	0.4421	1.13861
47.37806	0.38711	1.04683	52.9118	0.52697	0.96564
53.0312	0.72464	0.96412	56.42584	0.48049	0.92454
56.55851	0.83445	0.92312	61.97343	0.48636	0.87263
62.18996	0.8761	0.87088	73.26	0.5760	0.69094

Table 1. Inter planar Spacing parameters for PZLF8 and PLZF 10 samples

The Dislocation density

The dislocation density of the composites is estimated using the formula [26,27],

$$\delta = \frac{1}{D^2} \quad (3)$$

Where δ is dislocation density and D is the crystallite size.

The Results showing in Fig. 3 of the dislocation density of composites of PLZF8 and PLZF10 Wt% is calculated using equation (3). The observation made concludes that dislocation density decreases as particle size increases in both PZLF8 and PZLF 10.

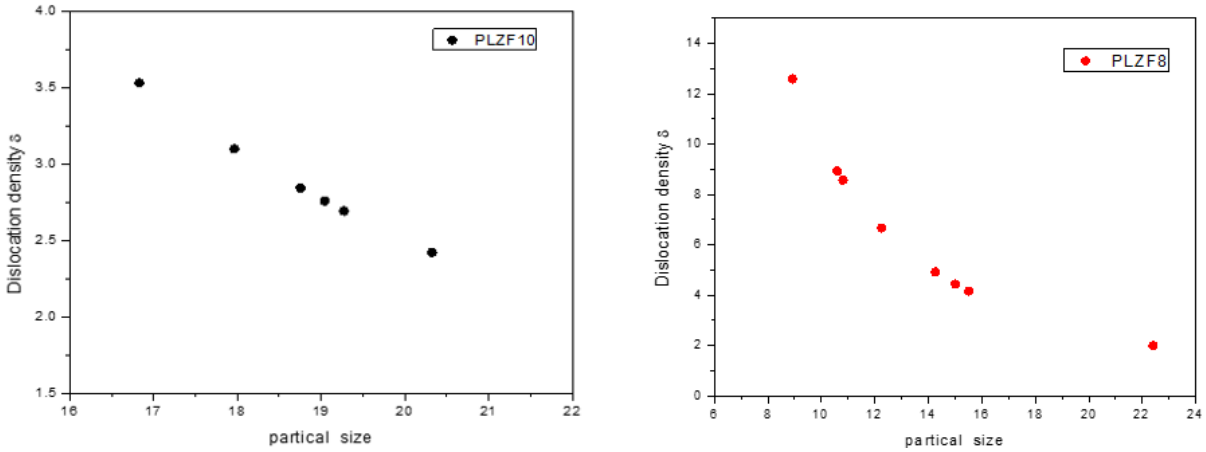

Fig. 3 of the dislocation density of composites of PLZF8 and PLZF10

Conclusions

The PPy/ $Li_{0.5-x/2}Zn_xFe_{2.5-x/2}O_4$ composites were synthesized successfully, The XRD characteristics showing crystalline nature confirms that formation of composites. The presence of additive to the polypyrrole sinks the date referred with JCPDS file (Card no. 89-1009).The crystallite size is calculated using Debye's Scherrer's equation and found to be 8.28 nm to 23.61 nm. Various crystallographic parameters including d-spacing hkl values of composite as well as have been calculated using Bragg's equation. EDAX study revealed that the lithium zinc ferrite oxide nanoparticles are evenly distributed throughout the polymer matrix. The morphological modification due to doping of $Li_{0.5-x/2}Zn_xFe_{2.5-x/2}O_4$ in Polypyrrole has resulted in the decrement in dislocation density decreases with the increase in particle size.

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