Research Paper

Preparation, Electrical and Optical Studies of ZnO Nanoparticles and Fe Doped ZnO Nanocomposites

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Abstract

ZnO nanoparticles and ZnO $_{(1\ x)}$ Fe$_{(x)}$ (x = 0, 0.25, 0.5, 0.75, 1gram) have been synthesized by chemical method. The pellets of ZnO nanoparticles and Fe doped ZnO nanocomposites were used for electrical and optical studies. The AC conductivity studies and dielectric stud-ies were carried out in the frequency range from 50Hz to 5MHz by using HIOKI 3532-50 LCR HITESTER Version 2.4. AC conductivity of the ZnO nanoparticle increases slightly in the low frequency region and it is almost a constant for a wide range of frequencies. At very high frequencies in the upper MHz region there is an abrupt increase in the conductivity. We observed that the dielec-tric constant decreases with the increase in concentration of Fe, the dielectric constant has high values in the low fre-quency regions for the nanomaterials. The structural and morphological studies of ZnO nanoparticles and Fe doped

ZnO nanocomposites were carried out using XRD and FTIR (3700-650cm ^{1}) analysis. In XRD pattern some

peaks appear in pure ZnO at higher angles disappear in the ZnO-Fe samples. This is because of the reduction of grain size and development of strain in the ZnO lattice by inducing Fe atoms. The calculated crystallite size for all the samples ranges from 20-30nm. FTIR studies suggest that the micro structural changes take place as a result of Fe doping in ZnO.

Keywords: Nanocomposites, AC conductivity, Di-electric, XRD, FTIR.

1 Introduction

Nanotechnology is dened as the study of manipulating matter on the atomic and molecular scale [1]. In General, nanotechnology deals with structures whose sizes vary be-tween 1 to 100 nm in one dimension at least, and involves developing materials having at least one dimension within that size range. It is able to create many new materials with a vast range of applications, such as in medicine,

biomaterials, electronics, and production of energy. How-ever, nanotechnology raises many concerns about toxicity and impact of nanomaterials on environment, and their eects on global economics.

Nanoparticles are particles that have one dimension that is 100 nanometers or less in size.The properties of many conventional materials change when formed from nanoparticles. This is typically because nanoparticles have a greater surface area per weight than larger par-ticles; this causes them to be more reactive to certain other molecules. Nanoparticles are used, or being evalu-ated for use, in many elds. Nanoparticles are of great scientic interest as they are eectively a bridge between bulk materials and atomic or molecular structures [2].

1.1 ZnO nanoparticles

ZnO, an inorganic compound also known as zincite, occurs rarely in nature, generally in a crystalline form. It usually appears as a white crystalline powder, which is nearly in-soluble in water. This has several favorable properties like high electron mobility, good transparency, wide bandgap for semi-conductivity, high room-temperature lumines-cence, etc. These properties are used in applications for electrodes in liquid crystal displays as well as in energy-saving and heat-protecting windows, electronic applica-tions of ZnO as thin-lm transistors and light-emitting diodes Zinc oxide has a stable wurtzite structure.

Zinc oxide has the wurtzite hexagonal crystal struc-ture. Commercial zinc oxides show this crystal structure only under electron microscopic examination. The pre-cise shape of the crystal depends on the method of forma-tion. In regular zinc oxide these vary between a cicular needles and plate shaped crystals. Zinc oxide can be in-duced to form a very large variety of crystalline shapes using specialized deposition methods, which is currently a very active area of research. Zinc oxide usually crystal-lizes in three dierent forms: hexagonal wurtzite, cubic zincblende and cubic rocksalt. The latter is the most rarely found. The wurtzite structure is most stable at ambient conditions and is hence most common [3].

2 Experimental: Materials and Preparation

2.1 Synthesis of ZnO nanoparticles (Chemical method)

The chemical reagents used in this work were Zn $(CH_3COO)_2.2H_2O$, NaOH and TEA of analytical grade purity. Zinc acetate solution was prepared by dissolving 0.001 mole of $CH_3COO)_2.2H_2O$ in 50 ml of water. The alkaline solution was prepared by dissolving NaOH (0.002 mole) and TEA (0.003 mole) in 250ml of absolute ethanol under stirring until a homogeneous solution is formed. The zinc salt solution was added into the alkaline solu-tion under magnetic stirring at 60-70 C and this solution was continuously heated for 2h at temperature 70 C. It was then allowed to cool naturally at room temperature.

After the reaction was complete, the resulting white product was washed with ethanol to remove the organic agent TEA and hydroxide ions. The product was ltered and dried in oven at 60-70 C [4].

2.2 Synthesis of Fe doped ZnO nanocomposites

The chemical reagents used in this work were Zn $(CH_3COO)_2.2H_2O$, $Fe(NO)_3.9H_2O$, NaOH and TEA of analytical grade purity. The solution was prepared by dissolving 0.001 mole of $Zn(CH_3COO)_2.2H_2O+Fe(NO)_3.9H_2O$ in 50 ml of water. The alkaline solution was prepared by dissolving NaOH (0.002 mole) and TEA (0.003 mole) in 250 ml of absolute ethanol under stirring until the homogeneous solution. The iron doped zinc salt solution was added into the al-kaline solution under magnetic stirring at 60-70 C and

this solution was continuously heated for 2h. It was then allowed to cool naturally at room temperature. After the reaction was complete, the resulting white product was washed with ethanol to remove the organic agent TEA and hydroxide ions. The product was ltered and dried in oven at 60 C for 2hr [4, 5].

2.3 Preparation of ZnO, ZnO-Fe pellet

For electrical conductivity measurements, the powder samples of ZnO nano particles/ZnO-Fe nano composites were pressed uniaxially into pellet of thickness 1-2mm and of diameter 12mm by applying pressure of 3 tons for 3 min using the device Polymerpress. The pellets were sintered at 100 C for 1h to get the thermal stability. Fine

quality silver paste was applied on both sides of the pellets for good electrical contacts.

3 Instrumentation

The pellets of ZnO nanoparticles and Fe doped ZnO nanocomposites were used for electrical and optical studies. The AC conductivity studies and dielectric studies were carried out in the frequency range from 50Hz to 5MHz by using HIOKI 3532-50 LCR HITESTER Version 2.4. The structural and morphological studies of ZnO nanoparticles and Fe doped ZnO nanocomposites were carried out using XRD and FTIR (3700-650cm $_1$) analysis.

4 Results and Discussion

4.1 Electrical Studies

The electrical properties of ZnO nanoparticles/ZnO-Fe nanocomposites pellets are inuenced mainly by the synthesis technique, grain size, cation distribution etc. In the present studies, dielectric and AC conductiv-ity studies have been undertaken on the prepared ZnO nanoparticles/ZnO-Fe nanocomposites. In particular,

measurement of AC conductivity studies and dielectric constant (^{0}) have been undertaken [6].

4.1.1 AC Conductivity

AC conductivity and Dielectric studies on the prepared ZnO nanoparticles has been undertaken using impedance analyzer model. The measurements were carried out at room temperature in between the range 100Hz-5MHz. Figure 1 shows the plots of AC vs frequency.

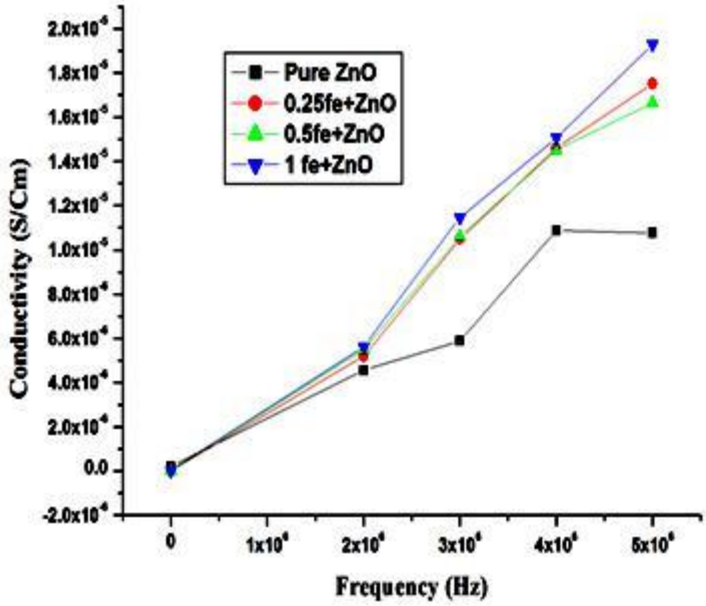

Figure 1: Plot of Conductivity versus Frequency of ZnO, ZnO-Fe Nanocomposite

4.1.2 Dielectric Studies

Figure 2 and Figure 3 show the variation of dielectric constant with log frequency for ZnO nano particle and ZnO-Fe nano composites. Pellets of ZnO and ZnO-Fe nano composite powders of thickness around 1.0 mm were made by applying a pressure of 3 ton in a polymer press. The measurements were carried out in the range from 50Hz to

5MHz. The dielectric constant ($_r$) of the ZnO and ZnO-Fe nano composite sample was determined by using the relation,

$$_r = \frac{Cd}{_oA}$$

Where C is the capacitance, d is the thickness, $_o$ is the permittivity of the free space (8.854 10 $_{12}$ F/m) and A is the surface area of the sample.

As the concentration of Fe increases dielectric constant decreases. The dielectric constant has high values in the low frequency regions for the nanomaterials than for the conventional materials. The very high values of dielectric constant at low frequencies may be due to the presence of dierent types of polarization mechanisms [7]. Because of the presence of interfaces in the nano materials, the appli-cation of an electric eld creates dipole moments and ro-tates them along the applied eld direction which is called as rotation direction polarization. Space charge polariza-tion and rotation direction polarization are responsible for the high value of dielectric constant for ZnO and ZnO-Fe nanomaterials at low frequencies [8].

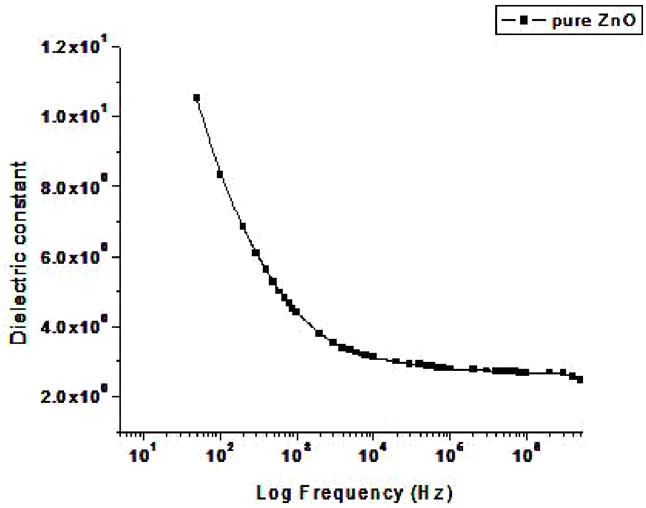

Figure 2: Plot of Dielectric constant versus Frequency of Pure ZnO nanoparticles.

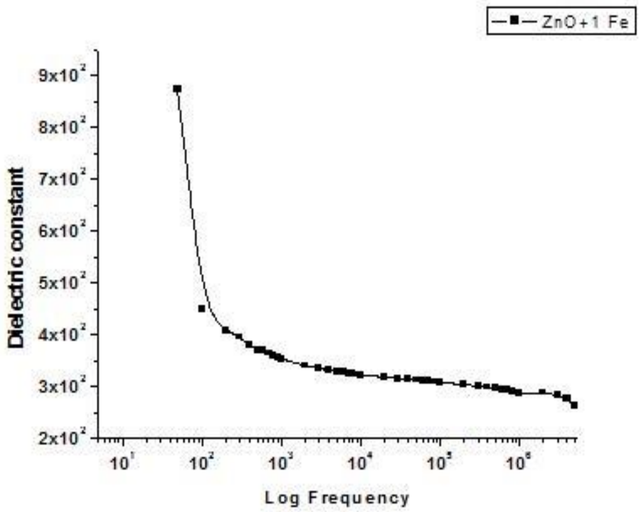

Figure 3: Plot of dielectric constant Versus Frequency of ZnO+1 Fe nanocomposite.

Table 1: Details of XRD data and crystallite size of ZnO+ 0.75 Fe nanocomposite.

Peak	2θ in degrees	Lattice spacing (d), Å	FWHM (degrees)	FWHM (radians), x10^{-3}	Crystallite size D, nm
1	31.681	2.82	0.367	6.40	22.49
2	34.344	2.60	0.343	5.98	22.23
3	36.174	2.48	0.360	6.28	23.20
4	47.455	1.91	0.416	7.26	20.85
5	56.498	1.62	0.406	7.08	22.20
6	62.762	1.47	0.442	7.71	21.04
7	67.837	1.38	0.446	7.78	21.45

4.2 XRD Studies

Figure 4 shows XRD patterns of ZnO-Fe sample. With increasing Fe concentration, the (1 0 1) or third peak ex-hibits an increase in line broadening.

It is also observed from the XRD patterns that impurity peak appears at higher angles in the ZnO-Fe samples. This is because of the reduction of grain size and devel-opment of strain in the ZnO lattice in inducing Fe atoms. The crystallite size (D) for all the samples was calculated using Scherrer's formula.

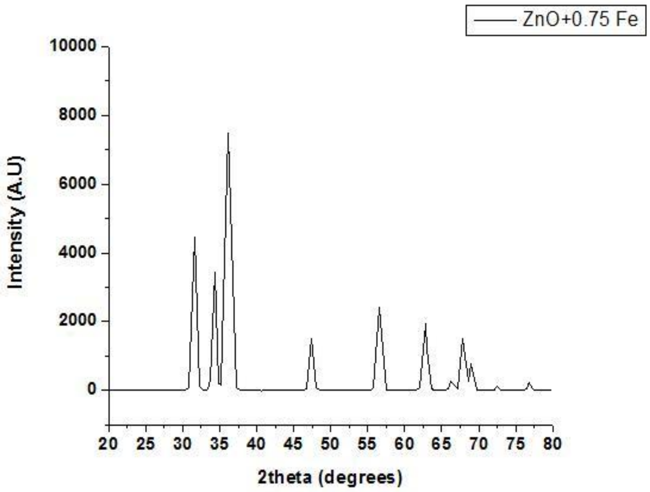

Figure 4: Plot of intensity versus 2 of ZnO+0.75 Fe nanocomposite.

4.3 FTIR Studies

FTIR spectra were recorded in solid phase using ATR technique in the wave number region 650-4000 cm $_1$ for ZnO and ZnO-Fe samples and are shown in Figure 5. This spectral region is very important because of several stretch modes involving hydroxyl bond, carbon-oxygen and metal oxide bonds are obtained clearly in this range.

Due to absorption of CO band at 1166.31 cm $_1$ (C-O) and a symmetric stretching vibration at 1388.86 cm $_1$ (COO) is observed. The band found at 1620.06 cm $_1$ is due to OH bond of water. The bending around 2838 cm $_1$ is because of absorption of CO_2 molecule present in air. The OH vibrations in ZnO lie in the range from 3000 to 3500 cm $_1$ depending on the conguration and number of hydrogen atoms absorbed by ZnO. Shifting of this band as a result of Fe doping suggests microstructural changes taking place in the ZnO matrix.

5 Conclusion

The AC electrical conductivity study shows that at con-stant temperature, for an increase in frequency, there is a slight increase in the electrical conductivity of the ZnO nanocomposite at the low frequency region and it is al-most a constant for a wide range of frequencies and at very high frequencies there is an abrupt increase in the conductivity. As the Fe concentration increases, AC con-ductivity increases as shown in Figure 6.

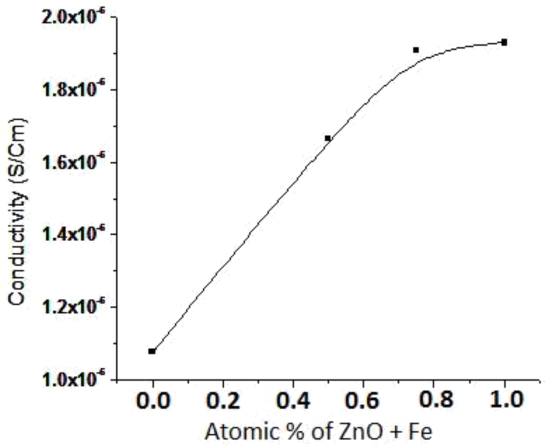

Figure 6: Plot of conductivity of ZnO-Fe nanocomposites at 5 MHz.

Table 2: Conductivity data of ZnO, ZnO-Fe nanocomposites at 5 MHz for all samples.

Sample	Conductivity at 5MHz (S/Cm)
PureZnO+0Fe	1.07719E-05
ZnO+0.25 Fe	1.75122E-05
ZnO+0.50,Fe	1.66475E-05
ZnO+0.75,Fe	1.90873E-05
ZnO+1,Fe	1.92952E-05

As the concentration of Fe increases, dielectric constant decreases. The very high values of dielectric constant at low frequencies may be due to the presence of dierent types of polarization mechanisms. XRD pattern shows that the reduction of grain size and development of strain in the ZnO lattice in inducing Fe atoms. FTIR spectra show the C-O bond and OH bond vibrations in ZnO nanoparticles and Fe doped ZnO nanocomposites. Shifting of the bands of Fe doped ZnO nanoparticles suggests microstructural changes taking place in the ZnO ma-trix.

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