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Zno-Bifeo$_3$ Nano Energy Materials for Advanced Applications

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ABSTRACT— Multifunctional zinc oxide-bismuth ferrite material was developed as energy material. The ferrite material was developed by employing polycrystalline $BiFeO_3$ and semiconductor ZnO via precipitation technique. The ZnO-$BiFeO_3$ composite was characterized by X-ray diffraction, scanning electron microscopy-energy dispersive spectroscopy, and transmission electron microscopy, which show that $BiFeO_3$ immigrated into the ZnO. Temperature dependent magnetic behavior of ZnO-$BiFeO_3$ composite was studied by vibrating sample magnetometer (VSM) in the range 5 to 300K. As temperature increased, the magnetic nature decreased; exhibiting a blocking temperature at 50K. This nanocomposite system has potentials for spintronics and energy applications.

KEYWORDS—Multifunctional; zinc oxide-bismuth ferrite and energy materials

I. INTRODUCTION

During the last two decades, the development of multifunctional nanomaterials has focused mainly, on their use for advanced energy applications due to their magnetic, electrical, optical and other characteristics [1, 2]. $BiFeO_3$ is a rhombohedra material and one of the multifunctional materials that show anti-ferroelectric, anti-ferromagnetism and anti-ferroelastic characteristics [3]. Owing to its functionality, semiconductor nature and significant bandgap (2.0-2.20 eV) and excitation binding drawn great attraction in energy applications [4], such as: electromagnetic sensors, memory devices and electric energy harvesting [5]. To enhance its applicability in materials science and nanotechnology [6], $BiFeO_3$ can be modified with suitable inorganic elements for pollutant degradation without any harmful residues. ZnO is one of the suitable inorganic compounds, that are nontoxic, with optimum transparency, direct bandgap [3.37eV], high excitation binding energy (60meV) and high electron mobility [200cm^{2}V^{-1}s^{-1}] etc [7]. Due to its positive characteristics, ZnO has been used for the development of good light-emitting diodes, electrode with a high quality Schottky contact for highly efficient higher electron mobility transistors, ultraviolet lasers, ultraviolet photodectors and nanostructured materials etc [7, 8].

Recently, many groups have attempted to address the efficient development of multifunctional energy systems for energy applications [9]. We et al [10] reported the development of dilayered $BiFeO_3$/ZnO thin films, which combination enhanced their functionality at increasing electrical field and temperature. The research group of Chen et al [11] reported the synthesis of $BiFeO_3$/ZnO core-shell heterostructures, using ZnO nanorod positive templates. In their investigation, $BiFeO_3$/ZnO nanorod arrays displayed enhanced coactivity and saturated magnetization when compared with signal $BiFeO_3$.
In this paper, precipitation technique was employed for the development of multifunctional zinc oxide-bismuth ferrite nanostructure materials using ZnO with $BeFO_3$, is reported. The zinc oxide-bismuth ferrite **[**ZnO-$BeFeO_3$] materials developed were characterized and evaluated for their temperature and magnetic field-dependent

applications. These core/shell materials have great potential for functional applications.

II. EXPERIMENTAL

A. Materials

Bismuth (III) nitrate pentahydrate, Iron (III) nitrate nanohydrate, zinc nitrate, ammonium hydroxide, nitric acid and potassium hydroxide were purchased from Sigma Aldrich Chemicals Company. All the chemicals were used as received, without purification. Distilled water was used during the complete experimental reaction.

B. Preparation of Zinc Oxide-bismuth ferrite (Zno-$BiFeO_3$) core/shell nanoparticles.

The preparation of ZnO-$BiFeO_3$ core/shell nanoparticles was achieved by following steps.

Step 1: Synthesis of single-phase bismuth ferrite ($BiFeO_3$): Bismuth ferrite was synthesized via a precipitation technique. 0.01M of bismuth (III) nitrate pentahydrate and 0.01M of iron (III) nitrate nanohydrate were completely dissolved in 100ml of diluted nitric acid (6.3ml HNO_3/93.7ml distilled water) solution in a 500ml beaker under the constant string condition, at ambient temperature. To this solution, potassium hydroxide was added slowly drop-wise in order to obtain a co-precipitate (Fe^{3+}, Bi^{3+} ions) until a brown color precipitate was formed during which the pH was adjusted to ~9. After starring for 30 minutes, the brown color precipitate obtained was filtered and washed with distilled water in order to remove the unwanted (K^+, NO_3^-) ions and the pH of filtrate was reduced to 7. The bismuth ferrite was dried at 120^{o}C for 2h. Finally, it was cooled to ambient temperature. Subsequently, the powders were dried and heat-treated at different temperatures.

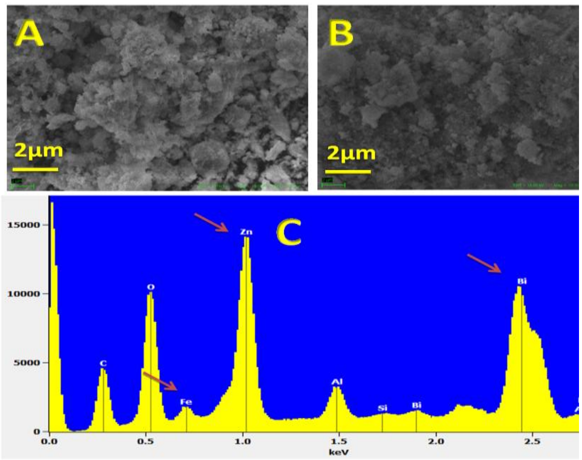


Fig 1: SEM image of A) $BiFeO_3$, B) ZnO-$BiFeO_3$ and EDS image of C) ZnO-$BiFeO_3$

Step 2: Zinc Oxide-bismuth ferrite (ZnO-$BiFeO_3$) nanoparticles:

Briefly, 14.87g of Zinc nitrate and different amounts (2-4g) of bismuth ferrite was dissolved in 50ml of distilled water under content stirring condition at ambient temperature for 1h. Subsequently, ammonium hydroxide solution was added drop-wise, until there was the formation of core/shell precipitation during which, the pH was adjusted to ~9. The core/shell precipitation was filtered and rinsed with distilled water 3 times. Finally, washed powder was dried at ambient temperature and cooled to ambient temperature. The powders were dried and heat-treated at different temperatures.

C. Characterizations

The ZnO-$BiFeO_3$ nanopowders developed were studied using X-ray diffraction, scanning electron microscopy-energy dispersive spectroscopy, transmission electron microscopy and also their temperature-dependent magnetic properties were determined by vibrating sample magnetometer.

III. RESULTS AND DISCUSSIONS

The morphology of the samples prepared were analyzed by using scanning electron microscope (SEM) and transmission electron microscope (TEM)) techniques. The SEM images of the nanoparticle metal oxides developed are presented in Fig 1. Fig 1A explains the fact that the **$BiFeO_3$** nanoparticles are not perfectly spherical, as they have nano-flower structure. Similar features have also been observed by Chybczynska et al [12].

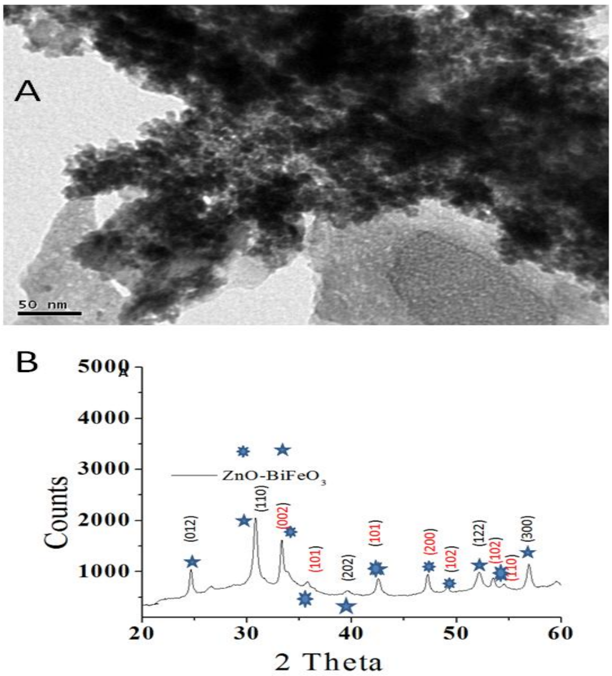
ZnO-$BiFeO_3$: Fig 1B shows the SEM image of the ZnO-$BiFeO_3$ core/shell developed, which is spherical in shape with highly agglomerated features. It is quite different when compared to Fig 1A. The image (in Fig 1A) explains the fact that $BiFeO_3$ nanoparticles were covered with ZnO nanoparticles. Energy dispersive spectroscopy (EDS) analysis (Fig 1C) shows clearly that Zn, Bi and Fe elements were present in the multifunctional materials. Therefore, the formation of multifunctional materials is confirmed by the SEM-EDS analyses.

In order to analyze the formation of core/shell nanoparticles, these powders were also analyzed by TEM. These studies also attested to the formation of ZnO-$BiFeO_3$ core/shell nanoparticles with spherical shape with highly agglomerated features, as shown in Fig. 2A. These results are mainly due to the strong interaction between the core/shell nanoparticles, which enhances their applicability in materials sciences and medical applications.

Analysis of the XRD patterns is a suitable technique for identifying the crystalline nature of the inorganic materials. Fig 2B shows the XRD pattern of ZnO-$BiFeO_3$ core/shell nanoparticles, synthesized via precipitation technique. The XRD pattern shows clear intensity peaks of ZnO-$BiFeO_3$ core/shell nanoparticles. The broad peaks identified at 2θ = 32.35º and 57.47º are the main characteristics of $BiFeO_3$ crystal planes (110) and (300), respectively [13]. The other diffraction peaks are highly significant to the formation of ZnO-$BiFeO_3$ core/shell nanoparticles [13-16].

Fig 2: TEM image of (A) ZnO-$BiFeO_3$ and (B) XRD pattern of ZnO-$BiFeO_3$

In order to investigate the nature of ferromagnetism in ZnO-$BiFeO_3$ nanocomposite, magnetic test was carried out on zero-field-cooling and field-cooling in the temperature range of between 5-300K. Fig. 3 shows the temperature-dependence of the zero-field-cooling and field-cooling magnetizations for ZnO-$BiFeO_3$, which exhibits a blocking behavior due to the very fine $BiFeO_3$ particles, supported by semiconductor ZnO. The zero-field-cooled magnetization of ZnO-$BiFeO_3$ sample shows a broad peak feature around 5K with decreasing order until 50K, the so-called blocking temperature (at 50K) and decreased thereafter from 100K to 300K. However, the field-cooled magnetization exhibited similar behaviour as zero-field-cooled magnetizations above blocking temperature. Thus, ZnO-$BiFeO_3$ system can be used for spintronics and energy applications in the range of 50K blocking temperature, which in future, can be achieved at room temperature by means of compositional modification.



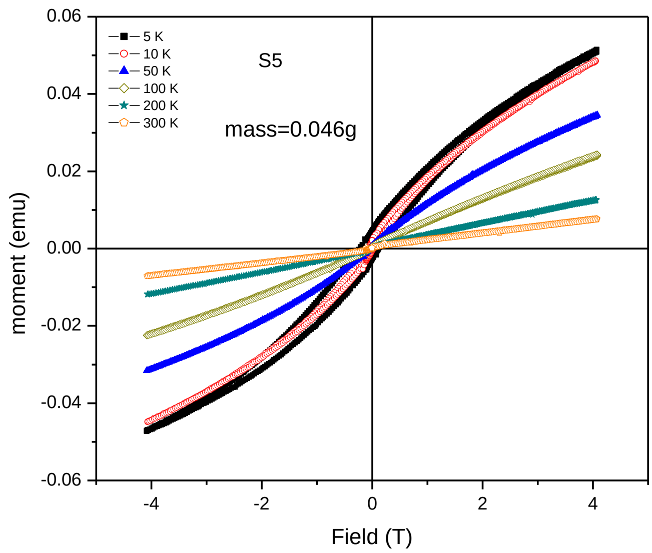


Fig 3: M-H curves of ZnO-$BiFeO_3$ at 300 and 5K

IV. CONCLUSION

In summary, semiconductor ZnO modified multiferroic $BiFeO_3$ nanocomposite system ZnO-$BiFeO_3$, with very fine particles, was prepared by precipitation method. Heat-treated powders were well crystalline, as supported by powder XRD studies showed temperature-dependent magnetic behavior (in the range of 5-300K) of with blocking temperature of ~50K, which is optimum composition for spintronic and energy applications.

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