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$BiFeO_3$-$MnFe_2O_4$ Nanocomposite with Multiferroic Properties

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Abstract— ***The BiFeO3-MnFe2O4 nanocomposite was prepared by simple chemical method through sol-gel route. The X-ray powder diffractometer was employed to identify the purity of desired phases in the composites using monochromatic CuKα radiation. The phase analysis confirms the mixed crystalline perovskite-spinel phases having rhombohedral-cubic structure. The frequency dependent dielectric measurements at room temperature were carried out using LCR meter (Agilent E4980A). The dielectric behavior of the multiferroic composite exhibits strong frequency dependency, where permittivity and loss declines as the frequency increases. Marine India PE-01 loop tracer was utilized for recording ferroelectric strength of the material by external electric field in the range of 0-6kV/cm at frequency of 50Hz. The P-E loop evidenced the ferroelectric polarization in the composite. The magnetic properties on the sample at room temperature were studied by M-H measurements in the field range of ±15kOe. The saturation magnetization was increased with the constituent ferrite content in the composite system. The ME coupling studies were done using lock-in amplifier set- up (Marine India). The BiFeO3-MnFe2O4 nanocomposite shows improved magneto-electric (ME) response in the composite. This possible improvement in magnetic and magneto- electric response makes the composite suitable for sensors and spintronic devices application.***

Index Terms— ***Multiferroic, nanocomposites, perovskite, spinel***

I. INTRODUCTION

Multiferroics are a special sort of multifunctional materials, which offers coexistence of magnetic, electric, and ferroelastic ordering. It has drawn future research directions due to its fascinating properties for various kinds of technological applications [1-2]. Single-phase multiferroic materials are not abundant with its magneto-electric effect. Therefore an intensive research work is being progressed for designing new materials having strong magneto-electric (ME) effect. The most promising single phase multiferroic system under extensive research is ABO3 perovskites. Multiferroic properties are achieved by introducing ferroelectric and magnetic cations in the A and B-site in these materials [3-4]. Perovskite BiFeO3 (BFO) having rhombohedral structure stands out as well known single phase multiferroic with its room temperature spontaneous ferroelectric and antiferromagnetic nature. It exhibits ferroelectric polarization 100μCcm^{-2} and Curie temperature of ~1100K [5-6]. The ferroic orders cross coupling in BiFeO3 is very weak and poor. The composite materials with good signal to noise ratio has been reported promising ME coupling coefficient provides tremendous device applications as magnetic field sensors, logic devices, switches, transducers etc [7-8].

The spinel ferrites has concerned as good magnetic material for technological applications because of its excellent physical and chemical features. It has low cost, appropriate dielectric loss and high efficiency which can be used in memory devices and sensors [9]. MnFe2O4 (MFO) has a inverse spinel structure having moderate magnetic saturation, good mechanical hardness, high permeability, low loss, good magneto crystalline anisotropy and has total spin moment 5 μB which is better than the other ferrites [10-11]. However, no work has been reported on BiFeO3-MnFe2O4 nanocomposite with its multiferroic properties using sol-gel route. Therefore, the present work reports BiFeO3-MnFe2O4 nanocomposite synthesis using sol-gel route and its multiferroic properties.

II. EXPERIMENTAL PROCEDURES

A. Synthesis of nanocomposites

A simple chemical method through sol-gel route is used to synthesize xBiFeO3-(1-x)MnFe2O4 nanocomposite. Stochiometric amount of Bi(NO3)3.5H2O, Fe(NO3)3.9H2O, Mn(NO3)2.4H2O, C6H8O7 and ethylene glycol were used for the preparation of composite in a typical procedure. The ratio of molar concentration of nitrates Bi:Mn:Fe were fixed at 1:9:19 were dissolved in the aqueous solution of citric acid and kept it at 70-80 ˚C with continuous stirring until a homogenous brown clear solution was formed. Then an appropriate amount of ethylene glycol, CA: EG=60:40 were added to this homogeneous mixture by maintaining same temperature and stirring until the viscous gel was achieved. Thereafter, the derived gel was kept at 110 ˚C in an oven for drying and calcined for 2hrs in air atmosphere at 600 ˚C. The resultant powder were grounded using pestle mortar and pelletised of 8mm diameter and 1mm thickness and kept for sintering for 2 hours at 700˚C making dense sample for electrical and magneto-electric coupling measurements.

The studies of structural, ferroelectric, dielectric, magnetic and magneto-electric coupling of the sample were done by different instrumental techniques. The X-Ray powder diffraction studies identified the crystallographic phase. The

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room temperature magnetic measurement of the sample upto ±15kOe was conducted using vibrating sample magnetometer. The permittivity and loss of the sample with frequency were carried out using LCR meter (Agilent E4980A). The ferroelectric nature of the composite was recorded using P-E loop tracer (Marine India PE-01). A lock in amplifier set-up has been used to record the magneto-electric response of the sample by AC and DC magnetic field.

III. RESULTS AND DISCUSSIONS

A. XRD Analysis

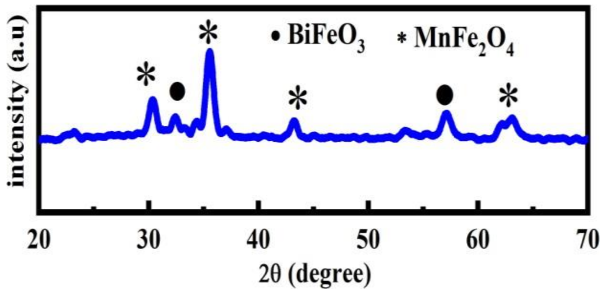

Fig. 1 XRD pattern of xBiFeO3-(1-x)MnFe2O4 nanocomposite

The XRD pattern of xBiFeO3-(1-x)MnFe2O4 nanocomposite at x=10% is shown in figure (1). The peaks (110) and (211) of BFO with perovskite rhombohedral structure (JCPDS card no72-2112) with symbol (●) and the peaks (220), (311), (400) and (440) of MFO with spinel cubic structure (JCPDS card no. 074-2403) with symbol (*). The XRD pattern confirms the presence of phase formation in the composite system. There are no unidentified peaks in the pattern reveals any unnecessary chemical reaction takes place during sintering [12]. The observed lattice parameters of ferrite phase (MnFe2O4) having spinel cubic structure and ferroelectric phase (BiFeO3) having perovskite rhombohedral structure are a=8.4 A˚ and a=3.95 A˚ respectively. The intensity of peak indicates the content percentage of constituent phases in the composite material. The average crystallite size 9nm of BFO and 8nm of MFO in the composite is estimated using Scherer's formula.

B. Magnetic Properties

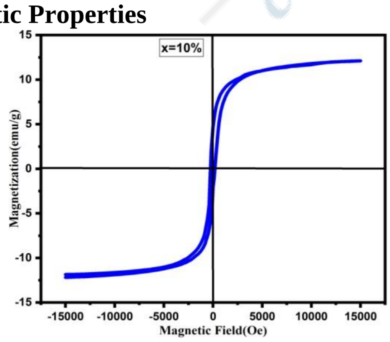

Fig. 2 M-H hysteresis loop of the xBiFeO3-(1-x)MnFe2O4 nanocomposite

The M-H hysteresis loop of the xBiFeO3-(1-x) MnFe2O4 nanocomposite at x=10% is recorded in the field range of ±15kOe at room temperature is shown in figure (2). It reflects typical ferromagnetic character and its saturation magnetization are observed to be 12emu/g. The sample gives better magnetization value than BFO (2.476 emu/g) by the addition of 90% of the composite partner MnFe2O4. Lots of works are published similar to our reports on bismuth ferrite and bismuth ferrite nanocomposites which are an anti-ferromagnetic multiferroic material with spiral spin structure exhibits low magnetization values. As manganese ferrite (MnFe2O4) is a soft ferromagnetic material with high magnetic saturation 110.6emu/g in bulk form and 66.89emu/g for pure nanoparticle [13], the addition of MFO to BiFeO3 resulted in increased magnetization of the composite as expected [14-15].

C. Dielectric Properties

The dielectric properties of the composite sample is explained by its permittivity and tangent loss. It varies with the change of temperature, frequency, humidity etc [16]. The figure 3(a) depicts frequency dependent variation of dieletric constant and loss of the composite from 100Hz to 2MHz. It shows decreasing permittivity and loss factor with increasing frequency. The Maxwell-Wagner's model and Koop's theory gives the description on this response. According to Koop's theory, highly resistive grain boundaries resist charge carriers motion accumulated at the interfaces in the low frequency region which makes dielectric loss very high. The high energy required large polarization at low frequency increases dielectric loss in the composite. It also depends the crystal defects and impurities in the material. The frequency dependent AC conductivity of the sample displays in the figure 3(b). In the low frequency regime, frquency independent plateau observed due to the bounded charges. As the frequency increases, conductivity increases shows little dispersion of charges [17- 18].

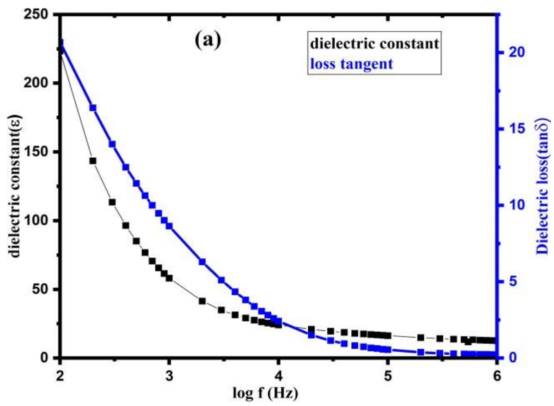

Fig. 3 (a) Variation of dielectric constant and dielectric loss of the nanocomposite with frequency

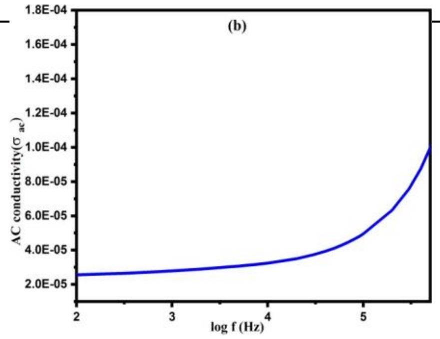

Fig.3(b) variation of frequency depedent ac conductivity of the composite.

D. Ferroelectric Properties

The ferroelectric behavior of composite at room temperature was examined by recording P-E loop with external electric field in the range of 0-6kV/cm. The figure (4) confirms the existence of ferroelectric order in the system. A bit round shaped hysteresis P-E loop indicates unsaturated polarization and very less ferroelectricity. It may be due to excessive leakage current in the composite and smaller electric field [19-20]. Here, the large concentration of MnFe2O4 in the composite matrix is also unfavourable and reduces polarization [21]. The effect of molar concentration of ferrite changes the FE properties of the composites will be presented in other communication in detail. However, the hysteresis loop reveals this nanocomposite is a typical ferroelectric nature of the BiFeO3-MnFe2O4 multiferroic composite system.

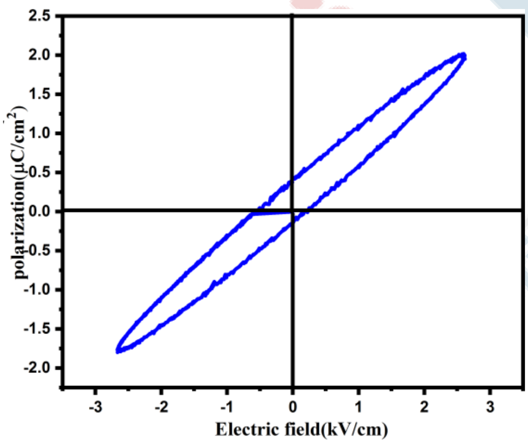

Fig. 4. P-E loop of the BiFeO3-MnFe2O4 nanocomposite

E. Magneto-electric coupling properties

The M-E coefficient system confirms the coupling performance between magnetic and ferroelectric phases in the composite. The ME coupling strength is estimated by magneto-electric voltage coefficient (αME) [22]. It was measured at constant Hac of 50Hz frequency by sweeping Hdc from 0 to 10kOe and at constant Hdc with sweeping Hac. The figure 5 (a) & (b) displayed ME voltage coefficient with sweeping Hdc/ Hac.

The enhancement of magneto-electric coupling could observe in the sample and the value of magneto-electric coefficient of the composite is 0.017 V/cmOe. It shows good ME effect in BiFeO3-MnFe2O4 composite due to its high polarization than pure BFO as compared with the earlier report [23-24]. The reported maximum value of ME coefficient of BFO is 0.002 mV/cmOe as per the literature. This study gives remarkable improvement in ME effect of BFO by combining with spinel MnFe2O4.

IV. CONCLUSION

In summary, multiferroic nanocomposite of BiFeO3-MnFe2O4 prepared using simple sol-gel route. The formation of spinel cubic structure of MnFe2O4 and perovskite rhombohedral structure of BiFeO3 was confirmed from XRD pattern by structural analysis. The magnetic hysteresis loop shows increment in the saturation magnetization value as compared with that of BFO by the addition of MnFe2O4. The dielectric behavior of the composite with frequency dependence showed the dispersion at low frequency regime. The existence of ferroelectric behavior in the composite is analyzed by recording P-E loop. The ME coupling measurements reports improved magneto-electric coupling response in BiFeO3- MnFe2O4 composite as compared to that of pure BFO [25-26].

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