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A systematic study of structural, magnetic and electric properties of perovskite-spinel composites prepared by sol-gel technique

Jarnail S. Bangruwa [a, b], Balesh Kumar Vashisth [a], Neelam Singh [c], Nidhi Singh [d], Vivek Verma [a, *]

[a] Department of Physics, Hindu College, University of Delhi, Delhi, India
[b] Department of Physics and Astrophysics, University of Delhi, Delhi, India
[c] Department of Physics, Maitreyi College, University of Delhi, Delhi, India
[d] CSIR-National Physical Laboratory, Dr. K.S. Krishnan Marg, Delhi, India

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ABSTRACT

Multiferroics composite of perovskite $BiFeO_3$ and spinel ferrites $NiFe_2O_4/ZnFe_2O_4/CoFe_2O_4$ with different composition were prepared by sol-gel method. Detailed investigations were made on the structural, magnetic and ferroelectric properties of these composites. The X-Ray Diffraction pattern confirms the formation of distorted perovskite and spinel phases of $BiFeO_3$ and $NiFe_2O_4$, $ZnFe_2O_4$, $CoFe_2O_4$ respectively. Transmission Electron Microscopy (TEM) images reveals the particle size and the elemental idea of phase formation. The particle sizes calculated using TEM of $NiFe_2O_4$, $ZnFe_2O_4$, $CoFe_2O_4$ are 10–20 nm, 20–30 nm, 15–25 nm respectively and these are compatible with XRD results. The results of Scanning Electron Microscopy (SEM) images reveal that all the samples exhibit a very uniform distribution of perovskite and spinel phases in composites. The modified microstructure of composites is effective in reducing the leakage of electric charges which occurs due to a chain formation of the spinel-ferrite phase particle, so the electrical, magnetic and ferroelectric properties of composites may improve with spinel ferrites content.

1. Introduction

Multiferroics is the class of materials which exhibits the ferroelectric and a magnetic order (ferromagnetism/ferrimagnetism/anti-ferromagnetism etc.) simultaneously. Recently the field of multiferroics attracted the extensive interest in the area of research and technology. The magneto-electric coupling between the electric and magnetic phenomenon, plays the very important role for applications point of view. This coupling enables the electrical polarization to be controlled by using the magnetic field and vice versa. $BiFeO_3$ (BFO) is one of the most important material which shows the multiferroic properties above the room temperature having transition temperature i.e. T_N (643 K) and T_C (1103 K). $BiFeO_3$ is reported to have a rhombohedrally distorted perovskite structure with *R3c* space group at room temperature [1–5]. But BFO exhibits the weak magnetoelectric response at room temperature which limited the technological importance of the material. There is the requirement of modifications in the material, so that we can achieve the high magneto-electric effect and enhance its multiferroic properties. Several studies have been carried out to improve the magnetic, electrical properties and prevent the formation of impurity phases in BFO materials. There are numerous ways like site engineering concept [6], composites of BFO with ferroelectric or magnetic materials [7], formation of thin films with lattice distortion on some substrates [8] through which we can achieve our aim. One of the effective ways to achieve the required properties of the multiferroic materials is to introduce the suitable materials (ferroelectric/ferromagnetic) with BFO to form the composites because generally composites show the better applications rather than single phase. $BiFeO_3$ is mainly the ferroelectric material and magnetic oxide materials like $NiFe_2O_4$ (NFO), $ZnFe_2O_4$ (ZFO) and $CoFe_2O_4$ (CFO) with high coerecivity, retentivity, magnetism and resistivity, can serve the purpose for our aim [9,10]. Hence, an effective way of enhancing the magnetic properties of BFO is to introducing suitable spinel ferrites to form multiferroic composites. The magneto electric coupling in these composites is also more

* Corresponding author.
E-mail addresses: vermavivek.neel@gmail.com, vivekverma@hinducollege.ac.in (V. Verma).

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pronounced than single phase BFO. Concurrently, the strong coupling between the different ferroic orders provides an additional degree of freedom in the design of sensors, actuators, magnetic recording media and spintronic devices etc. [11–13]. Among the various methods available for synthesis of materials, Sol-gel technique is used very often for the synthesis of most of the inorganic materials [14]. In this study, a sol-gel procedure is used for the synthesis of pure and perovskite-spinel composites. In the present work, the perovskite-spinel interface effect on the structural, ferroelectric and magnetic properties are under investigation in view of the enhancement of multiferroicity.

2. Experiment

2.1. Preparation of nano bismuth-ferrite

In recent years, the sol-gel technique has emerged as a versatile method for synthesizing different inorganic materials. Apart from the advantage of low temperature synthesis a sol-gel route make it possible to obtain pure phase materials. Pure BFO was successfully synthesized by the sol-gel technique [15,16]. The precursor solutions were prepared by using highly pure $Bi(NO_3)_3 \cdot 5H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$, as the starting materials and distilled water as a solvent. The stoichiometric ratios of these materials were dissolved in the distilled water and HNO_3 (2 ml) to form the aqueous solutions. Citric acid (1:1 molar ratio of metal ions) was subsequently added as a complexing agent in an appropriate proportion to the above solution under constant stirring. The resultant solution was then evaporated and dried at approximately 80 °C on a hot plate under continuous stirring to obtain xerogel powders. Then the xerogel powders were grinded in the agate mortar. The obtained powder samples were annealed at 600 °C for 4 h in order to obtain the pure phase of BFO.

2.2. Preparation of nano spinel-ferrites

Pure $NiFe_2O_4$ (NFO), $ZnFe_2O_4$ (ZFO) and $CoFe_2O_4$ (CFO) samples were synthesized using the sol-gel technique. The raw materials used in the process were highly pure $Fe(NO_3)_3 \cdot 9H_2O$, $Zn(NO_3) \cdot 5H_2O$ $Ni(NO_3) \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$. The stoichiometric amounts of these starting materials were dissolved in the distilled water and HNO_3. Citric acid (1:1 molar ratio of metal ions) was used to serve the purpose of complexing agent. Citric acid was added to the aqueous solutions in appropriate amount under constant stirring. On complete dissolution of the precursors ammonia solution was added to adjust the pH = 7 of solutions. The resultant solutions were then evaporated and dried at ~80 °C on a hot plate under constant stirring. The mesoporous solid structure swollen with liquid (gel) was then converted to xerogel powders. These xerogel powders were ground in the agate mortar followed by annealing at 400 °C for 1 h.

2.3. Preparation of composites

Multiferroic composites (1-x)BFO-xNFO, (1-x)BFO-xZFO, (1-x) BFO-xCFO for x = 0, 0.1, 0.2 and 0.3 i.e. 0.9BFO-0.1NFO (BFO-NFO 1), 0.8BFO-0.2NFO (BFO-NFO 2), 0.7BFO–0.3NFO (BFO-NFO 3), 0.9BFO-0.1ZFO (BFO-ZFO 1), 0.8BFO-0.2ZFO (BFO-ZFO 2), 0.7 BFO–0.3ZFO (BFO-ZFO 3) and 0.9BFO-0.1CFO (BFO-CFO 1), 0.8BFO–0.2CFO (BFO-CFO 2), 0.7 BFO–0.3CFO (BFO-CFO 3) were prepared by sol-gel auto-combustion method. For the formation of composite, first we dissolved require amount of $Bi(NO_3)_3 \cdot 5H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ in distilled water with the constant magnetic stirring followed by the addition of dilute HNO_3. Citric acid was added to the aqueous solutions in appropriate amount under constant stirring. Solution was kept under the constant stirring at 80 °C till gel formation. After gel formation, a required amount of nano-ferrites (NFO/ZFO/CFO) was added in different beakers to form the composite. Same procedure was followed for all compositions. After formation of xerogel, powders were grounded in the agate mortar and then annealed at 600 °C for 4 h. The annealed powders were subjected to a hydraulic press (10 ton) after mixing them with PVA solution. The well dense pellets (diameter ~ 8 mm & thickness ~ 1 mm) thus obtained were sintered at 700 °C for 5 h. The pellets were silver coated for the electrical characterization. The structural analysis was carried out by Brucker D 8 Discover, X-ray diffractometer (XRD) using CuKα as radiation source with wavelength 1.5406 Å in a wide range of Bragg angles 2Θ (20°–70°) at a scanning rate of 2° per minute. Particle size measurement was carried out by using Transmission Electron Microscopy (Tecnai G^2 T30, U-Twin FEI Netherlands). The surface morphology of the samples was characterized by Scanning Electron Microscopy (JEOL Japan Mode JSM 6610 LV). The room temperature magnetic measurements were performed with vibrating sample magnetometer (Lakeshore-7410). The room temperature ferroelectric measurements were performed by using the Automatic P-E Loop Tracer (Marine India).

3. Results and discussion

3.1. Analysis of nano-$BiFeO_3$, $NiFe_2O_4$, $ZnFe_2O_4$, $CoFe_2O_4$

Fig. 1 shows the X-ray diffraction pattern of pure $BiFeO_3$, $NiFe_2O_4$, $ZnFe_2O_4$, and $CoFe_2O_4$ samples. It may be noted that the obtained peak corresponding to the planes (012), (104), (110), (006), (024), (116), (122), (220) was similar to the JCPDS 71-2494 for BFO single phase perovskite structure. Only one impurity peak about $2\theta = 28°$ (shown by *) was observed. These impurities are always obtained during the synthesis of $BiFeO_3$ due to its chemical kinetics. It can be seen that XRD presents the diffraction peaks at reflection planes indexed (220), (311), (222), (400), (511), (333), (440) for all the spinel ferrite samples indicating the single phase cubic spinel structure. All the peaks in XRD pattern could be identified as that of $NiFe_2O_4$, $ZnFe_2O_4$ and $CoFe_2O_4$. The average crystallite size of samples was calculated by using Scherrer's formula $D = 0.9\lambda/\beta \cos\theta$, where D is the mean crystallite size, λ wavelength of Cu Kα, β is the full width at half-maximum (FWHM) of the diffraction peaks and θ is Bragg's angle. It was observed that the average crystallite size of $NiFe_2O_4$, $ZnFe_2O_4$, $CoFe_2O_4$ are 20 nm, 16 nm, 17 nm respectively. Fig. 2 shows the transmission electron

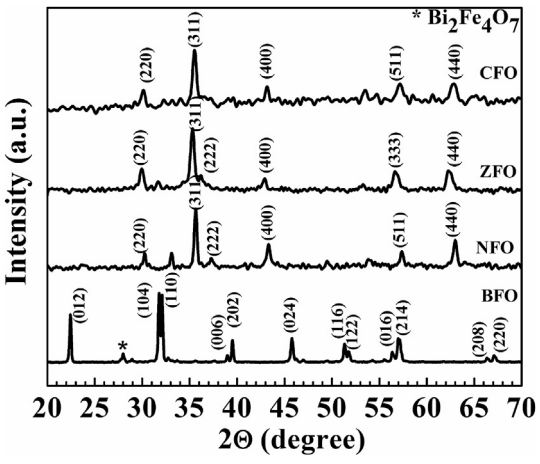

Fig. 1. X-Ray Diffraction pattern of pristine $BiFeO_3$, $NiFe_2O_4$, $ZnFe_2O_4$ and $CoFe_2O_4$ samples.