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Nanocomposite electroceramics with ferroelectric and ferromagnetic responses

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Abstract

$Bi_{3.4}Nd_{0.6}Ti_3O_{12}$ and $CoFe_2O_4$ were synthesized by chemical solution route. Multilayer structures (two, four, and ten alternate layers) of $CoFe_2O_4/Bi_{3.4}Nd_{0.6}Ti_3O_{12}$ were deposited on Pt substrate ($Pt/TiO_2/SiO_2/Si$) by spin coating. X- ray diffraction of multilayer structures reveals composite-like polycrystalline film. Leakage current of the composite ten multilayers was less than 10^{-6} A and Ohmic-like bulk response up to electric field 120 kV/cm, showed the co-existence of ferroelectric polarization (P_r) > 47 μC/cm^2 and ferromagnetic memory (M_r) > 400 emu/cm^3 at room temperature. FE and FM coupling in the same material can be attributed to stress different permeability and permittivity of the materials involved.

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Keywords: multiferroics; composites; $CoFe_2O_4/Bi_{3.4}Nd_{0.6}Ti_3O_{12}$; spin coating; ferromagnetic; ferroelectric

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1. Introduction

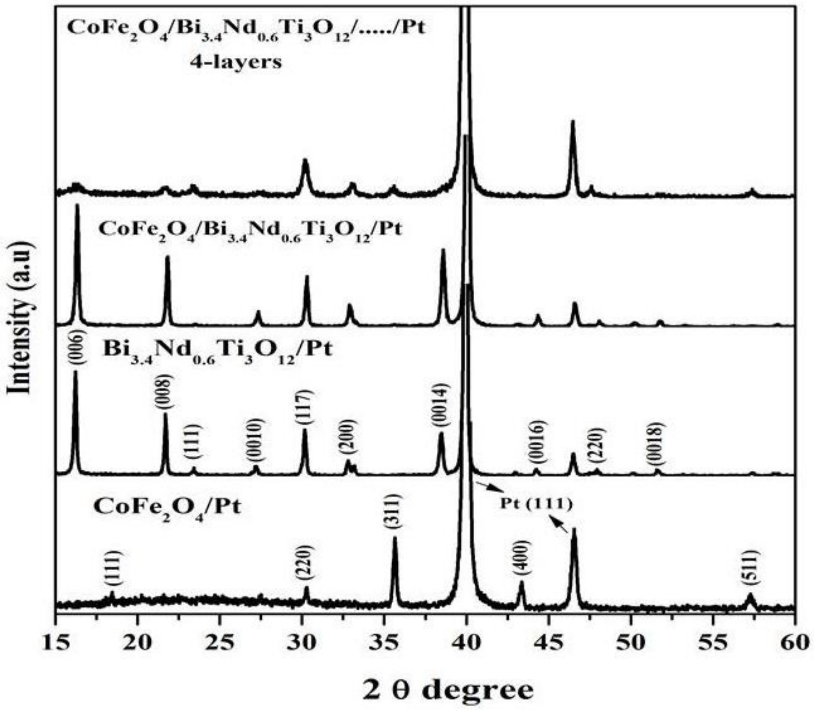
Magnetoelectric coupling in a material is important for the development of multifunctional devices [1, 2], and the co-existence of multiferroic property in the same material system may also have interesting applications. The unusual properties and fascinating underlying physics could lead to new devices such as coupled FeRAMs (ferroelectric random access memories) and MRAMs (magnetic random access memories), non-linear magneto-optical devices, surface acoustic wave devices, and tunable capacitors and sensing application. Aurivillious phase compound system consists of $(Bi_2O_2)^{2+}$ $(A_{n-1}B_nO_{3n+1})^{2-}$, where A is mono, di, or trivalent cations, B is cation with valence 4, 5 or 6, and n is the number of perovskite layers [3, 4]. $Bi_4Ti_3O_{12}$ is one of compound in Aurivillious family of monoclinic ferroelectric structure with one component of polarization in the plane of the layers and the other component perpendicular to this plane and shows low ferroelectric polarization. If Bi^{3+} ions in A-site is partially substituted by trivalent cation, a solid solution of the type $Bi_{4-x}M_xTi_3O_{12}$ (M = La^{3+}, Nd^{3+}, Sm^{3+}) have shown large spontaneous ferroelectric polarization [5-8]. $BaTiO_3$ is perovskite ferroelectric and $CoFe_2O_4$ is well known ferrimagnetic material with spinel structure. Alternate layers of $BaTiO_3$-$CoFe_2O_4$ multilayer structures prepared by pulsed laser deposition (PLD) have been investigated [2] in order to study the ferroelectric (FE) and ferromagnetic (FM) coupling. Recently, ferroelectric (FE) and ferromagnetic (FM) responses have been demonstrated in $CoFe_2O_4/Bi_{3.4}La_{0.6}Ti_3O_{12}$ composite structure [9]. For a better understanding of the process-structure-property, we studied $CoFe_2O_4/Bi_{3.4}Nd_{0.6}Ti_3O_{12}$ structures deposited on Pt substrate ($Pt/TiO_2/SiO_2/Si$) by spin coating. We report here the synthesis, structural properties, leakage current, and ferroelectric (FE) and ferromagnetic (FM) responses $CoFe_2O_4/Bi_{3.4}Nd_{0.6}Ti_3O_{12}$ multilayer structures at room temperature.

2. Material Synthesis

Bismuth nitrate pentahydrate $Bi(NO_3)_3.5H_2O$, niodium nitrate hexahydrate $Nd(NO_3)_3.6H_2O$ and titanium isopropoxide $C_{12}H_{28}O_4Ti$ were used as precursors for Bi, Nd, Ti, respectively for the formation of 0.08 molar solution of $Bi_{3.4}Nd_{0.6}Ti_3O_{12}$. Cobalt (II) nitrate hexahydrate $CoN_2O_6.6H_2O$ and iron (III) nitrate hydrate $FeN_3O_9.9H_2O$ were used as precursors for Co and Fe respectively, to achieve 0.2 molar solution of $CoFe_2O_4$. To prepare $Bi_{4-x}Nd_xTi_3O_{12}$ precursor solution, bismuth nitrate (10 mol % excess) and niodium nitrate were dissolved in 2-methoxyethanol solvent and stirred at room temperature for 1 hour. Titanium isopropoxide was dissolved in 2-methoxyethanol and stirred for 30 min and both solutions were mixed and stirred finally for 12 h to achieve homogeneous and transparent solution. To prepare the $CoFe_2O_4$ solution, cobalt nitrate and iron nitrate were dissolved in 2-methoxyethanol and stirred for 12 h at room temperature. These solutions were kept in separate Pyrex bottles. The solution containing $Bi_{3.4}Nd_{0.6}Ti_3O_{12}$ was spin coated at 5000 rpm for 20 s on Pt substrate. As the temperature of phase formation of $Bi_{3.1}Nd_{0.6}Ti_3O_{12}$ and $CoFe_2O_4$ is around 750° C, each coated layer was dried on a hot-plate at 400° C for 5 min. Then, coated film was rapid thermal annealed at 750° C for 15 min in oxygen environment. The solution containing $CoFe_2O_4$ was similarly coated, dried and annealed at 750° C on $Bi_{3.4}Nd_{0.6}Ti_3O_{12}$ covered surface. The structure was given a final rapid thermal anneal at 750° C for 5 min. Total thickness was measured by profilometer (260 nm for bilayer and 510 ± 10 nm for four alternate layers).

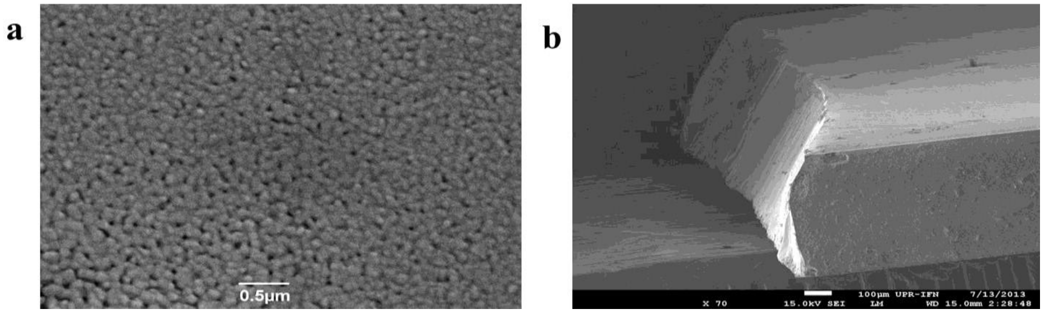
3. Results and Discussion

Alternate layers of $CoFe_2O_4/Bi_{3.4}Nd_{0.6}Ti_3O_{12}$ were deposited by spin coating on Pt substrate ($Pt/TiO_2/SiO_2/Si$). The x-ray diffractions patterns of two and four alternate layers are shown in Fig. 1 (Rigaku Cu-Kα radiation, 0.1540 nm). For comparison purpose, the x-ray diffraction patterns of individual $CoFe_2O_4$ and $Bi_{3.4}Nd_{0.6}Ti_3O_{12}$ films, labeled by JPCD data base, are also shown in figures 1.



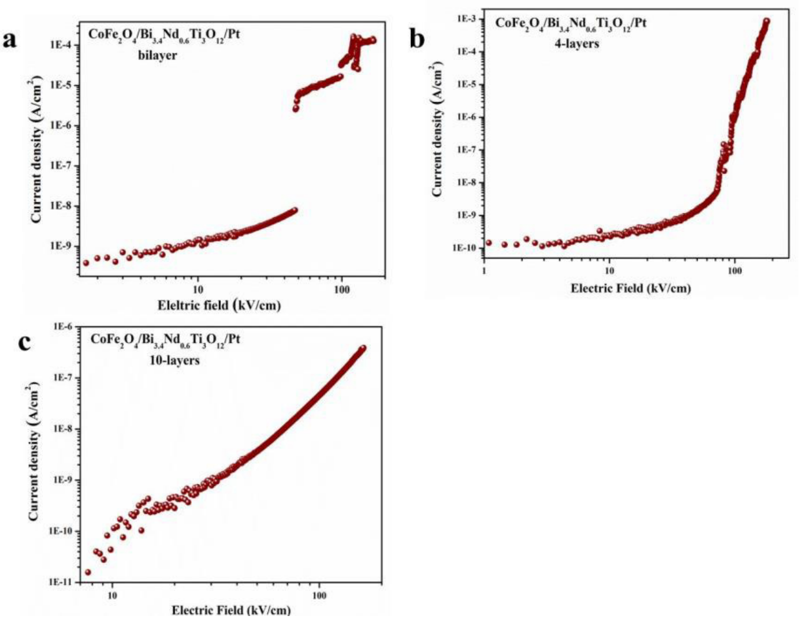
Figures 1. X-ray diffraction patterns of pure $CoFe_2O_4$ and $Bi_{3.4}Nd_{0.6}Ti_3O_{12}$ thin films, and $CoFe_2O_4$ /$Bi_{3.4}Nd_{0.6}Ti_3O_{12}$ multilayers on Pt substrate

Dominant peaks (006), (008) and (0014) of $Bi_{3.4}Nd_{0.6}Ti_3O_{12}$, and (311) and (511) peaks of $CoFe_2O_4$ co-exist in $CoFe_2O_4$/$Bi_{3.4}Nd_{0.6}Ti_3O_{12}$ alternate layers. It indicates a composite–like structure with c-axis staggered growth of one on another. Figure 2 (a) shows the scanning electron microscopy (SEM) images of the films with grain sizes of 10 to 100 nm, and the SEM cross-sectional image of the film on Pt substrate with uniform deposition by spin coating.



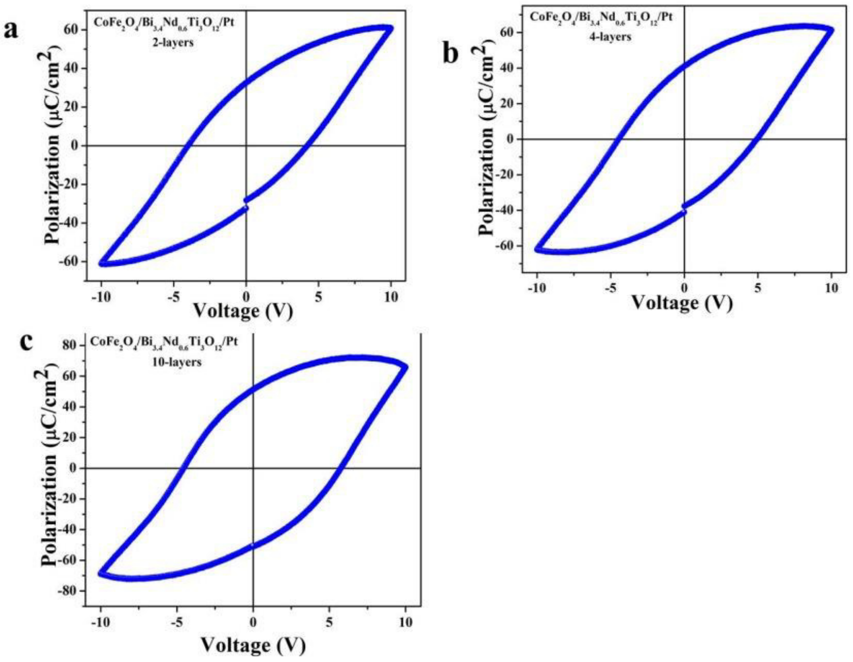
Figures 2. (a) Scanning electron microscopy (SEM) show the of the surface morphology (b) show the cross sectional images

For electrical measurements, the top electrode of Pt (3 x10^{-4} cm^2) was deposited on the film by dc sputtering using mechanical mask. Thus, Pt electrodes were used on both sides in a capacitor structure. figure 3 (a, b and c) show the leakage current as a function of applied dc electric field using digital electrometer (Keithley 6514) on two, four, and ten alternate CoFe$_2$O$_4$/Bi$_{3.4}$Nd$_{0.6}$Ti$_3$O$_{12}$ layers. In very thin films, tunneling is expected, and grain boundaries can give rise to inflection in intermediate fields. But, space charge limited current (SCLC) and electrode-film interface resistance may dominate at larger fields. One can observe similar behavior of leakage current vs applied electric field measurements on ~ 200 nm thick bilayer film shown in figure (3 a), where the leakage current is less than 10^{-8} A up to the electric field up to 100 kV/cm, and inflexion occurs in intermediate field region followed by the dielectric breakdown for thin bilayer structure. As the film thickness increases, tunneling can be ruled out and bulk behavior is expected to dominate as revealed in figure (3 b), where leakage current is mostly bulk Ohmic type. Similar behavior was also observed [6-8] in Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ electroceramic films. But, in very thick film (ten layers) only bulk behavior dominated even at relatively higher electric fields as observed in figure (3 c).

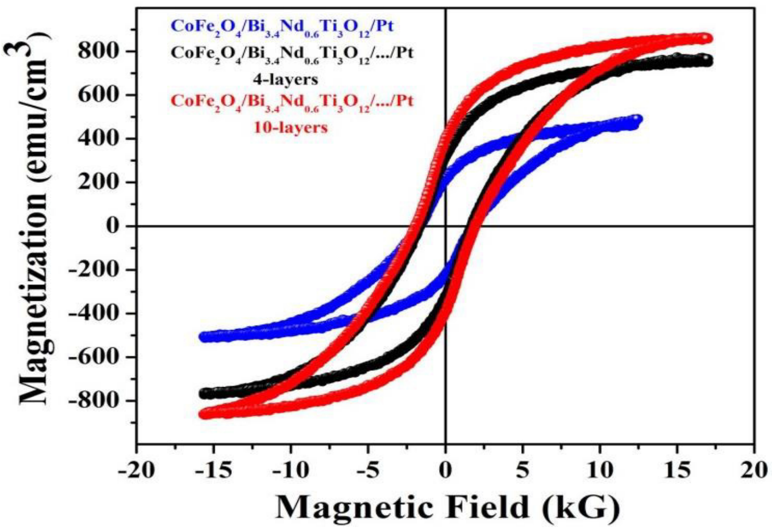


Figures 3. Leakage current versus electric field of the CoFe$_2$O$_4$/Bi$_{3.4}$Nd$_{06}$Ti$_3$O$_{12}$ (a) two, (b) four, and (c) ten, alternate layers

The ferroelectric (FE) responses were measured by RT 6514 HVS tester on Pt/film/Pt capacitor configuration using FE probe (Radiant Technologies, NM). Figures 4 (a, b, c) shows FE hysteresis curves at room temperature with remnant polarization (P$_r$) ~ 30, 37 and 47 μC/cm^2, respectively on two, four and ten alternate layers. The observed increase in P$_r$ with increased multilayers indicates a composite-like property but crystalline anisotropy cannot be ruled out. The ferromagnetic (FM) responses were measured by vibrating sample magnetometer (VSM 7400 series. Lake Shore, CA) and are shown in figure 5. One can observe the room temperature FM hysteresis with magnetization (M$_r$) ~ 200, 240, and 380 emu/cm^3, respectively on two, four, and ten-alternate layers. The increased value of the measured M$_r$ with increased layers also indicates the composite-like FM property without film segregation. Although, the origin of the co-existence of FE and FM in the same material system is not yet clear, stress in multilayer structure and different permeability and permittivity of the materials involved, can be attributed to FE and FM coupling. Role of the substrate-film interface, effect of grain boundaries, and effect of electric field on magnetization is under investigation.



Figures 4. FE hysteresis loop of (a) CoFe$_2$O$_4$/Bi$_{3.4}$Nd$_{0.6}$Ti$_3$O$_{12}$ two (b) CoFe$_2$O$_4$/Bi$_{3.4}$Nd$_{0.6}$Ti$_3$O$_{12}$ four and (c) CoFe$_2$O$_4$/Bi$_{3.4}$Nd$_{0.6}$Ti$_3$O$_{12}$ ten, layers



Figures 5. Magnetization hysteresis loop of CoFe$_2$O$_4$/Bi$_{3.4}$Nd$_{0.6}$Ti$_3$O$_{12}$ two (blue), four (black), and ten (red) layer structures

4. Conclusion

$CoFe_2O_4$ and $Bi_{3.4}Nd_{0.6}Ti_3O_{12}$ were synthesized by chemical solution route, and multilayers were deposited on Pt substrates by spin coating. XRD revealed the formation of composite-like structures. Leakage current below 10^{-6} A shows ohmic-like behavior in low fields (< 90 kV/cm) and inflection in intermediate field have been observed in very thin structure. Composite-like FE and FM property is evident, e.g. $P_r > 37$ μC/cm^2 and $M_r > 240$ emu/cm^3 for four-layer structure and higher P_r and M_r for ten-layer structures were achieved at room temperature. Simultaneous appearance of FE and FM is attributed to stress in multilayer structures.

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