



Effect of rare earth substitution on properties of barium strontium titanate ceramic and its multiferroic composite with nickel cobalt ferrite



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ABSTRACT

Effect of substitution of rare earth ions (Dy^{3+} , Gd^{3+} and Sm^{3+}) on various properties of $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{TiO}_3$ (BST) i.e. the composition $\text{Ba}_{0.95-1.5x}\text{Sr}_{0.05x}\text{TiO}_3$ (where $x = 0.00, 0.01, 0.02, 0.03$ and R are rare earths Dy, Gd, Sm) and that of their multiferroic composite with $\text{Ni}_{0.8}\text{Co}_{0.2}\text{Fe}_2\text{O}_4$ (NCF) has been studied. Shifting of peaks corresponding to different compositions in the X-ray diffraction pattern confirmed the substitution of rare earth ions at both Ba^{2+} and Ti^{4+} sites in BST. It is clear from scanning electron microscopy (SEM) images that rare earth substitution in BST increases its grain size in both pure and composite samples. Substitution of rare earth ions results in increase in value of dielectric constant of pure and composite samples. Sm substitution in BST significantly decreases its Curie temperature. Dy substituted pure and composite samples possess superior ferroelectric properties as confirmed by polarization vs electric field (P–E) loops. Composite samples containing Dy, Gd and Sm substituted BST as ferroelectric phase possess lower values of remanent and saturation magnetizations in comparison to composite sample containing pure BST as ferroelectric phase (BSTC). Rare earth substituted composite samples possess higher value of magnetoelectric coefficient as compared to that for BSTC.

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1. Introduction

Multiferroic composites belong to a special class of materials which exhibit magnetoelectric effect i.e. enhancement of electric polarization in magnetic field and magnetization in electric field, as a product property [1]. Weak magnetoelectric coupling in single phase multiferroic materials (BiFeO_3 , BiMnO_3) [2] inhibits the use of these materials in practical applications such as magnetic field sensors, microwave devices (transducers, filters, phase shifters, oscillators), memory devices, spintronic devices, etc. Multiferroic composites solve this problem as they possess strong coupling between electric and magnetic fields via strain. This is the main reason of progressing research in this area. A ferrimagnetic material of high magnetostrictive coefficient is homogeneously mixed with a ferroelectric material of high piezoelectric coefficient to obtain multiferroic composite possessing high magnetoelectric coefficient. Recently Sharma et al. [3] synthesized $\text{BiFeO}_3\text{--CoFe}_2\text{O}_4$ nanocomposites using sol–gel process and studied their ac conductivity and magnetic properties. Mandal and Nath [4] prepared $\text{Co}_{0.65}\text{Zn}_{0.35}\text{Fe}_2\text{O}_4\text{--PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ composites via sol–gel method followed by microwave sintering and reported that microwave

sintered composites possess high magnetodielectric effect in comparison to conventional sintered composites. Mudinepalli et al. [5] studied enhanced magnetodielectric properties in lead free $\text{Ni}_{0.83}\text{Co}_{0.15}\text{Cu}_{0.02}\text{Fe}_{1.9}\text{O}_{4-\delta}\text{--Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ composites by spark plasma sintering. In addition to these, large number of multiferroic composites such as $\text{BiFeO}_3/\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ [6], $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3/\text{CoFe}_2\text{O}_4$ [7], $\text{PMN-PT}/\text{Co}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ [8], $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3/\text{BaTiO}_3$ [9] has also been explored. Ferrimagnetic materials as nickel ferrite, cobalt ferrite, nickel zinc ferrite and nickel cobalt ferrite possess smaller resistivity as compared to ferroelectric materials such as barium titanate, barium strontium titanate, barium zirconium titanate, lead zirconium titanate [10], etc. To obtain magnetoelectric coupling in these composites, dielectric properties are compromised because on mixing ferroelectric and ferromagnetic phases of multiferroic composites overall dielectric constant of these composites decreases as compared to that of ferroelectric material. Therefore some solution is required to enhance dielectric constant of multiferroic composites. Rare earth ions such as Dy^{3+} , Gd^{3+} , Sm^{3+} , when substituted in small proportions, are known for enhancement of overall dielectric constant in Barium titanate [11]. Fewer reports (mostly in single phase multiferroic material BiFeO_3) deal with effect of rare earth doping on multiferroic properties. Mukherjee et al. [12] reported enhancement in multiferroic properties on doping of rare earth ion Gd^{3+} in BiFeO_3 . Xu et al. [13] studied the

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improvement in magnetic and ferroelectric properties in Dy doped BiFeO₃. Singh et al. [14] reported the enhancement of magnetoelectric coupling in SmFeO₃-PbTiO₃ (Pb_{0.8}Sm_{0.2}Ti_{0.8}Fe_{0.2})O₃ solid solution. To the best of our knowledge so far there are no studies available that provides insight on the effect of rare earth doping in barium strontium titanate on various properties of multiferroic composites based on it. This investigation provides a comprehensive study on effect of substitution of Dy³⁺, Gd³⁺, Sm³⁺ ions on various properties of barium strontium titanate (Ba_{0.95}Sr_{0.05}TiO₃) as well as that of its multiferroic composite with nickel cobalt ferrite (Ni_{0.8}Co_{0.2}Fe₂O₄).

2. Experimental details

Ba_{0.95-1.5x}Sr_{0.05}R_xTiO₃ (where $x = 0.00, 0.01, 0.02, 0.03$ and R are Rare earths Dy, Gd, Sm) has been synthesized by solid state reaction method using analytical grade of BaCO₃, SrCO₃, R₂O₃ and TiO₂ as precursors. These materials were ball milled with zirconia balls in distilled water for 24 h and slurry thus obtained, was dried in oven at 120 °C. The mixture was calcined at 1150 °C in box furnace. Solid state preparation of nickel cobalt ferrite (Ni_{0.8}Co_{0.2}Fe₂O₄) has already been mentioned in our earlier publication [15].

Multiferroic composites have been prepared by mixing 0.85 Ba_{0.95-1.5x}Sr_{0.05}R_xTiO₃ and 0.15 Ni_{0.8}Co_{0.2}Fe₂O₄ (NCF) powders using ball milling in acetone with zirconia balls for 12 h. Pure Ba_{0.95-1.5x}Sr_{0.05}R_xTiO₃, Ni_{0.8}Co_{0.2}Fe₂O₄ and composite powders were pelleted with poly vinyl alcohol (PVA) as binder and sintered at 1200 °C for 6 h. X-ray diffraction analysis of sintered pure and composite powders has been carried out using Rigaku Miniflex II. Microstructural analysis of sintered samples has been performed using scanning electron microscopy (SEM) by Zeiss MA15. Density of sintered samples was measured using Archimede's principle. Silver paste was applied on flat sides of sintered pellets for making electrical contacts to measure dielectric properties. Dielectric properties of pure and composite sintered samples were measured using impedance analyzer Wayne Kerr 6500B in frequency range of 20 Hz–1 MHz and temperature range of 50–160 °C. Ferroelectric properties were investigated by recording polarization vs electric field (P-E) loops using sawyer-tower circuit at 25 °C. Magnetic properties of multiferroic composite samples were measured using vibrating sample magnetometer (VSM). Magnetoelectric properties were measured by dynamic method at room temperature. For simplification, sintered samples of Ba_{0.95-1.5x}Sr_{0.05}R_xTiO₃ with R as Dy³⁺, Gd³⁺, Sm³⁺ are represented respectively by DN, GN, SN (N = 1, 2, 3 for $x = 0.01, 0.02, 0.03$ respectively) and representation of corresponding composite samples is DNC, GNC, SNC. BST and BSTC are respectively the notations used for Ba_{0.95}Sr_{0.05}TiO₃ and its composite.

3. Results and discussion

3.1. X-ray diffraction analysis (XRD)

Indexed XRD patterns clearly indicated the formation of single phase tetragonal perovskite and inverse spinel structures in Ba_{0.95-1.5x}Sr_{0.05}R_xTiO₃ (Fig. 1a(i)) and Ni_{0.8}Co_{0.2}Fe₂O₄ (Fig. 1b) respectively (see Fig. 1c).

Enlarged view of highest peak in Fig. 1a(i) is shown in Fig. 1a(ii). Vertical straight line is drawn in the figure to estimate the shifting of different peaks corresponding to various compositions with respect to the centre of peak corresponding to BST. There is an unsymmetrical shift of peaks corresponding to different proportion of Dy, Gd and Sm substitution. Peaks corresponding to composition $x = 0.01$ & $x = 0.03$ in case of all the three substitutions Dy, Gd and Sm are shifted towards higher angles with respect to the centre of peak corresponding to BST and that for composition $x = 0.02$ are shifted towards lower angles. Shifting of peaks towards lower and higher angles respectively indicate an increase and decrease of lattice constant in those compositions with respect to that for BST. This shifting of XRD peaks can be explained in terms of ionic radius of rare earth ions. Ionic radius of different ions taken from Shannon's table [16,17] in 12 and 6 coordination is listed in Table 1.

Rare earth ions Dy³⁺, Gd³⁺ and Sm³⁺ can occupy both the A and B sites in the perovskite ABO₃ type structure depending on tolerance factor (t), such that it nearly equals to unity [17–19], and ratio of A and B ions [20,21]

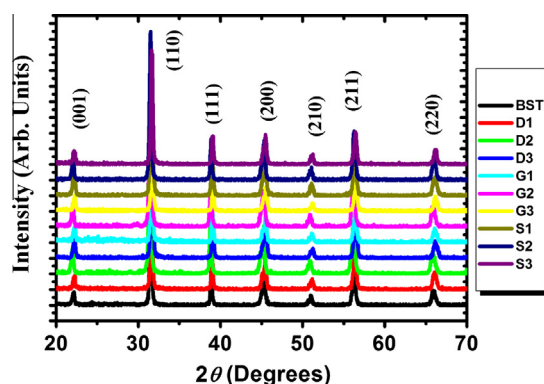


Fig. 1a(i). XRD pattern of BST and its Dy, Gd and Sm substitutes.

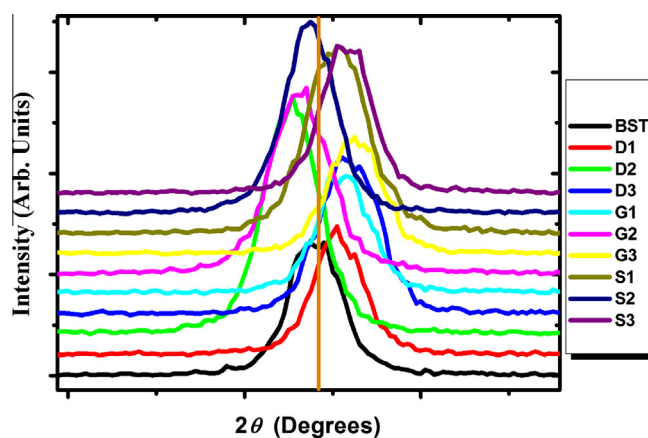


Fig. 1a(ii). Enlarged view of highest peak in XRD pattern of BST and its Dy, Gd and Sm substitutes.

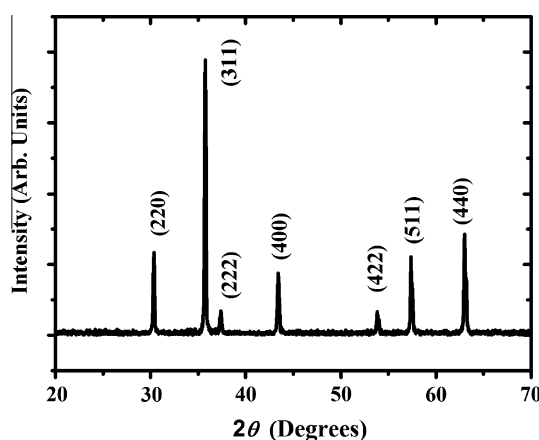


Fig. 1b. XRD pattern of NCF.

$$t = (r_A + r_O) / \sqrt{2}(r_B + r_O) \quad (1)$$

where r_A , r_B and r_O are respectively atomic radii of ions at A, B and O site. Dy³⁺, Gd³⁺ and Sm³⁺ ions firstly have the tendency to occupy Ba²⁺ site than Ti⁴⁺ site for their smaller proportions [22–24]. Decrease in lattice parameter for D1, G1 and S1 samples as compared to BST implies the replacement of larger Ba²⁺ by smaller Dy³⁺, Gd³⁺ and Sm³⁺ ions. For the compositions D2, G2 and S2, rare earth ions prefer replacing Ti⁴⁺ ions than Ba²⁺ ions, resulting into increase in lattice constant as ionic radii of rare earth ions is larger

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