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Investigating the effect of multiple grain–grain interfaces on electric transport behavior of [50 wt% $BaFe_{12}O_{19}$–50 wt% $Na_{0.5}Bi_{0.5}TiO_3$] magnetoelectric nanocomposite system

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ABSTRACT

Polycrystalline [50 wt% $BaFe_{12}O_{19}$ (BaM)–50 wt% $Na_{0.5}Bi_{0.5}TiO_3$ (NBT)] particulate novel magnetoelectric nanocomposite system was successfully fabricated by solid state reaction technique. The Rietveld refinement of X-ray diffraction pattern was provided the evidence about the pure phase formation of desired nanocomposite system as well as the presence of both ferrimagnetic (FM) BaM & ferroelectric (FE) NBT phases separately. The Field Scanning Electron Micrograph (FESEM) and Scanning Tunneling Electron Micrograph (STEM) explored the information about grain size and connectivity of the composite system. The XPS study was helped to examine the presence of oxygen vacancy (O_v) as well as multi oxidation states of transition metal ions for nanocomposite system.

In this report we have systematically examined the conduction mechanism of different interfaces (BaM-BaM, BaM-NBT and NBT-NBT) by the help of complex impedance spectroscopy technique. From our investigation it was observed that, different interfaces activates at different temperature ranges. Due to absence of O_V, BaM-NBT interfaces conduction dominants over BaM-BaM interfaces conduction even at room temperature (RT). The mechanism behind the appeared high dielectric loss ($tan\delta$) at RT which was reduced when NBT-NBT interfaces were activates at higher temperature was explained by Maxwell-Wagner type interfacial polarization concept.

1. Introduction

In this rapid development of wireless communication era, the fabrication of new nano ceramics are necessitates for high efficiency multifunctional devices at room temperature. Magnetoelectric mutiferroic composite systems have drawn the significant attention for both commercial and research communities due their large magnetoelctric coupling as well as giant dielectric constant than single phase multiferroic systems [1]. For a two phase composite system there are ten different connectivity schemes can possible (0–0, 1–0, 2–0, 3–0, 1–1, 2–1, 3–1, 2–2, 3–2, and 3–3) where their distributions as well as connectivity plays crucial role on the magnetic, electric as well as magnetoelectric coupling properties [2]. The strain meditated coupling-physics-mechanism between anti- or ferroelectric (piezoelectric) and anti- or ferromagnetic (magnetostrictive) order parameters in magnetoelctric composite systems offers various potential applications such as: multiple-state memory elements, electric-field controlled ferromagnetic (FM) resonance devices, sensors, transducers, spintronics and terahertz emitters, miniature antennas, etc [1,3–5]. Therefore, around the world several magnetoelectric mutiferroic ceramic composite systems with different geometries combinations such as: $BaTiO_3$–$Ni_{0.7}Zn_{0.3}Fe_2O_4$ [6], $CoFe_2O_4$-$Pb_{0.7}Ca_{0.3}TiO_3$ [7], $Na_{0.5}Bi_{0.5}TiO_3$-$CoFe_2O_4$ [8], $Ni_{0.5}Zn_{0.5}Fe_2O_4$–$Pb(Zr_{0.53}Ti_{0.47})O_3$ [9],$Na_{0.5}Bi_{0.5}TiO_3$-$CoFe_2O_4$ [10], $CaCu3Ti_4O_{12}$-$NiFe_2O_4$ [11],0.1$Ni_{0.8}Zn_{0.2}Fe_2O_4$–0.9$Pb_{1-3x/2}Sm_xZr_{0.65}Ti_{0.35}O_3$ [12],($Ni_{0.3}Cu_{0.4}Zn_{0.3}Fe_2o_4$)-[50%batio$_3$+50%PZT] [13], $Li_{0.5}Ni_{0.75-x/2}Zn_{x/2}Fe_2O_4$-$Ba_{0.5}Sr_{0.5}TiO_3$ [14],Terfenol-D-$LiNbO_3$ [15], Terfenol-polyvinylidene fluoride [16], 0.9$Pb(Zr_{0.52}Ti_{0.48})O_3$–0.1$Pb(Zn_{1/3}Nb_{2/3})$O3 multilayer composite [17], Terfenol-D-epoxy pseudo-1–3 magnetostrictive composite plates on two longitudinally polarized PZT/epoxy 2–2 piezoelectric composite plates [18], $CoFe_2O_4$ ferromagnetic microstrips embedded in (K,Na)NbO_3-based piezoceramic substrate [19], $PbTiO_3$-$SrFe_{12}O_{19}$ [20], $BaTiO_3$–$BaFe_{12}O_{19}$ [21], $(PbZr_{0.65}Ti_{0.35}O_3)0.97$–$(BaFe_{12}O_{19})0.03$ [22] have been explored by different research groups.

But, one of the major drawbacks in the emerging field of multiferroics is the trustworthy detection of intrinsic magnetoelctric cou-

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pling (MEC) from frequency vs. magneto capacitance data. Because occasionally magnetoresistance (MR) combined with the Maxwell-Wagner effect that provides a mechanism for magneto-capacitance in the system which is not necessarily intrinsic MEC [23]. This problem can quite avoidable by considering magneto impedance (MI) spectroscopic study which can segregate intrinsic MEC and extrinsic magnetoresistance effect [24,25]. However, the magnetoresistance (MR) effect for a composite system (which is purely interfaces effect) is also useful for analysis of spin-polarized tunneling mechanism at ferromagnetic(FM)-Insulator(I)-ferromagnetic(FM) interfaces which is essential for spintronics and magneto impedance sensor applications [26–29]. Likewise, the concept behind the interfacial charge induced magnetoelectric coupling for a magnetoelectric composite system based upon coupling at ferromagnet-insulator interface due to spin-dependent screening, where an applied electric field produces accumulation or depletion of spin-polarized electrons resulting in a change of the interface magnetization [30–32]. So here we can argue that, the general prediction of mutiferroic behavior for a composite system will be incomplete without understanding the individual interfaces conduction mechanism. Because different grain-grain interfaces (FM-FM, FM-FE and FE-FE) having different activation energies (different resistive and capacitive nature). Therefore conduction mechanism study of individual interfaces can improve the understating of mutiferroic behavior, spin-polarized tunneling mechanism as well as interfacial magnetoelectric coupling for a magnetoelectric composite system.

Previously few researchers were attempted to study the conduction mechanism of muliferroic composite systems with the help of impedance spectroscopic technique, without considering the individual conduction mechanism of different interfaces [33–36]. Recently, we were successfully extracted the significant effect of different interfaces (BaM-BaM, NBT-NBT and BaM-NBT) on conduction mechanism of bulk [50 wt% $BaFe_{12}O_{19}$–50 wt% $Na_{0.5}Bi_{0.5}TiO_3$] magnetoelectric composite system in different temperature ranges [37]. But we were found less resistive nature of bulk composite system than bulk BaM and NBT systems which may be unsuitable for practical applications. But from various studies it can be found that the electric and magnetic properties of a ceramic systems can be improve by reducing the grain size (to the nano range) [38–41]. It was well known that due to large surface area to volume ratio and smaller dimensions, nanostructures appear to be promising candidates for chemical sensors working at various temperatures and also increasingly important role towards modern technologies such as: information processing and storage to spin electronics, communication devices and electrical power generation than bulk system [42]. It was also found that, magnetically hard/soft exchange-coupled nanocomposites show enhanced magnetic properties (high magneto crystalline anisotropy or magnetically hard) due to inter-grain exchange interactions have immense potential applications in green energy, power electronics, and data storage applications etc. [43–45]. Recently in magnetoelectric nanocomposite system it was observed that, the magnetic anisotropy can be tailor by an adjacent ferroelectric material which may explore a new device concepts, such as electric-field controlled magnetic data storage [46]. Therefore we have concluded the fabrication of nano systems, were not only improving the applicative properties than bulk but also inventing new physics/effects which was fully absent in bulk systems.

So to achieve, better electric and magnetic applicative properties, the present work was devoted towards the fabrication of nano grain size [50 wt% $BaFe_{12}O_{19}$–50 wt% $Na_{0.5}Bi_{0.5}TiO_3$] composite system and extracting of different interfaces effect on conduction mechanism by help of complex impedance spectroscopy technique which may explore the better understanding towards multiferroic properties as well as magnetoelectric coupling interaction in future.

2. Experimental details

The 50 wt% $BaFe_{12}O_{19}$–50 wt% $Na_{0.5}Bi_{0.5}TiO_3$ nanocomposite system was synthesized by conventional solid state technique. For synthesis of our desired composite nanocomposite system, at first we have prepared polycrystalline nano $BaFe_{12}O_{19}$ by auto combustion technique considering stoichiometry amount of $Ba(NO_3)_2$ and $Fe(NO_3)\cdot 9H_2O$ as precursors where glycine ($C_2H_5NO_2$) used as fuel. After combustion, the combusted powder was calcinated at 900 °C for 12 h for getting the pure phase of $BaFe_{12}O_{19}$ (BaM). Likewise polycrystalline nano $Na_{0.5}Bi_{0.5}TiO_3$ was synthesized by using a modified sol–gel method, which is called the solution/sol–gel (SSG) method [47]. By this method at first stoichiometry amount Bismuth oxide (Bi_2O_3) and Sodium carbonate (Na_2CO_3) were dissolved into nitric acid (HNO_3) then add ethylene glycol ($HOCH_2CH_2OH$) and stirrer slowly at 70 °C until the solution looks pale yellow. A stoichiometry amount of titanium tetraisopropoxide $Ti(OCH(CH_3)_2)_4$, was then added to the solution, and the mixture was stirred at 70 °C for 2 h at last blackish color powder was collected. Then the powder was calcinated at 775 °C for 8 h and gone for verification the formation of pure phase of NBT by X-ray diffraction (XRD) technique.

Then the calcined $BaFe_{12}O_{19}$ (BaM) and $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) powders were mixed in weight percentage 50:50 wt% thoroughly by grinding. Then polyvinyl alcohol (PVA) used as a binder in the BaM–NBT mixed powder pressed into cylindrical pellets of 10 mm diameter and 1 mm thickness & sintered at 790 °C for 8 h. For dielectric measurement of nano BaM and NBT system the calcined powders were sintered (after making pellets by above procedure) at 940 °C and 790 °C for nano BaM and NBT systems respectively. The formation of the desired nano composite system, nano BaM and nano NBT systems was verified by XRD using DMAXB/Rigaku in a wide range of Bragg angles 20–80° (step size as 0.002) with Cu Kα radiation (λ=1.5405 Å). The surface morphology of different systems was studied from Field emission scanning electron microscopic (FESEM) images (taken by Nova NanoSEM-450 Field emission scanning electron microscope system) and Scanning tunneling microscopic image (STEM) (taken by FEI TECNAI F30 G2 STWIN 300 kV system). The dielectric parameters, i.e. impedance, and phase angles, were measured in a wide frequency range 100–1 MHz and temperature range 30–200 °C using HIOKI IMPEDANCE ANALYZER 1352. The Room temperature X-ray photoelectron spectroscopy (XPS) studied by (S/N: 10001, Prevac, Poland) spectra were taken with AlKα (hν=51,486.6 eV) radiation and a hemispherical energy analyzer.

3. Results and discussion

Fig. 1a shows the XRD patterns corresponds to pure phase formation of nano BaM, nao NBT and nanocomposite systems with absence of any other impurity phases. The position of observed peaks was verified with corresponding JCPDS pattern. As our focused study on nano composite system then we were done Rietveld refinement for nanocomposite system. Fig. 1b shows the XRD pattern (Y_{obs}) observed for nano composite system. A standard computer program FullProf Suite Toolbar was utilized for Rietveld refinements. The theoretical fitted (Y_{cal}) data proves that, obtained XRD pattern contains both ferrimagnetic (FM) BaM and ferroelectric (FE) NBT ordering phases without presence of any impurity phase. The refined structural parameters such as R_p (profile fitting R-value), R_{wp} (weighted profile R-value), R_{exp} (expected weighted profile factor) and S (goodness of fit) $=(R_{wp}/R_{exp})$ obtained after refinement are given in Table 1.

The FESEM micrograph (Fig. 2a and b) illustrates the dense nano grains (≤140 nm for BaM and ≤125 nm for NBT) were homogeneously distributed throughout the system for both nano BaM and NBT system. Fig. 2c shows the dense microstructure of nanocomposite system having grain size approximately ≤230 nm which are homogeneously distributed throughout the system. To confirm the grain size we have