

Properties of $(x)\text{CoFe}_2\text{O}_4-(1-x)\text{BiFeO}_3$ multiferroic composites

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Abstract: The crystal structure and optical as well as electromagnetic properties of multiferroic $(x)\text{CoFe}_2\text{O}_4-(1-x)\text{BiFeO}_3$ ($x=0.0\div 0.5$) composites prepared by solid state reaction method have been systematically investigated. The XRD analysis indicated that both spinel CoFe_2O_4 (CFO) and perovskite BiFeO_3 (BFO) phase simultaneously exist in the sintered composite. Absorption spectra showed the optical band gap of these composites decreases slightly with the increase of CFO concentration. In the Raman spectra, the peaks showed the different weights of CFO phase respect to BFO phase. Magnetization curve showed the coercivity H_c value of composites increases with increasing the CFO concentration and achieves the highest squareness M_r/H_c of about 11.12 % with $x=0.4$. The impedance spectroscopy of CFO-BFO composites exhibited that the strong dielectric property of composite was still well maintained with $x=0.4$. These results suggest that the electromagnetic property of CFO-BFO composite is optimized with x of about 0.4.

Keywords: Multiferroic, composites, perovskite, spinel, impedance

1. Introduction

The term multiferroic is used to describe the materials in which both ferromagnetic order and ferroelectric order occur simultaneously at the same time. This material is currently the subject of intensive scientific investigation because these materials potentially offer a whole range of new device application [1] such as spin valves, which change electric resistance depending on the direction of applied magnetic field, and multiple approach-memories, in which data can be stored or read in terms of electric polarization by means of the application of a magnetic field, giving rise to non-destructive memory storage and reading [2]. However, there are few multiferroic systems existing in nature at room temperature because ferroelectric and ferromagnetism tend to be mutually exclusive. There are some methods to synthesize room temperature multiferroic materials, in which to create the combination of two effects magnetostrictive and piezoelectric in composite materials is hoped to bring the largest magnetoelectric respond [3-7]

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BiFeO_3 material, a rhombohedrally distorted perovskite, has long been known as a multiferroic material with ferroelectric ($T_c=1103$ K) and G -type antiferromagnetic ($T_N=643$ K) properties [8]. The high spontaneous polarization of $6.1 \mu\text{C}/\text{cm}^2$ along [111] direction and $3.5 \mu\text{C}/\text{cm}^2$ along [100] direction are reported in BiFeO_3 single crystals [9]. Spinel CoFe_2O_4 is a well-known hard magnetic material, which has been studied in detail due to its high coercivity (5400 Oe) and moderate saturation magnetization (about 80 emu/g) as well as its remarkable chemical stability and mechanical hardness [10]. Spinel – perovskite $(x)\text{CoFe}_2\text{O}_4-(1-x)\text{BiFeO}_3$ ($x=0.0\div 0.4$) composites prepared by sol-gel technique was reported by Shao-Yun Fu et al [11]. The nanocomposites with composition $0.3\text{CoFe}_2\text{O}_4-0.7\text{BiFeO}_3$ annealed at 700°C exhibited the largest coercivity H_c of 1351 Oe and the optimal squareness M_r/M_s of 54 %. The saturation magnetization M_s and coercivity (H_c) increase drastically with the increase of CoFe_2O_4 concentration in the nanocomposites annealed at 700°C . $\text{Bi}_{0.8}\text{La}_{0.2}\text{FeO}_3/\text{CoFe}_2\text{O}_4$ pulsed laser deposition multilayer thin films also were prepared by Shan-Tao Zhang et al. [6] which exhibited the ferroelectric loops with P_r and P_s of 4.3 and $13.3 \mu\text{C}/\text{cm}^2$. On the other hand, the films showed well-shaped magnetization hysteresis loops with M_s and M_r of 34.7 and $11.4 \text{emu}/\text{cm}^3$, respectively.

In this paper, we present a study on spinel – perovskite $(x)\text{CoFe}_2\text{O}_4 - (1-x)\text{BiFeO}_3$ ($x=0.0\div 0.5$) composites prepared by solid state reaction technique and an investigation on the crystallographic structure and optical as well as electromagnetic properties of these composites to find out the optimal concentration of CFO in $(x)\text{CFO}-(1-x)\text{BFO}$ composites.

2. Experimental

The CFO-BFO composites were fabricated by two- step solid-state- reaction method. The constituting spinel CFO powder was prepared by stoichiometrically mixing CoO and Fe_2O_3 powders and calcining the mixture at 700°C for 6h. Similarly, the perovskite BFO powder was separately prepared by thoroughly mixing Bi_2O_3 and Fe_2O_3 and calcining the resulting mixture at 700°C for 6h. CFO and BFO were ball-milled, pressed specimens then calcined the second time at 800°C for 8h. The two constituting oxides were then mixed with the molar ratio of CFO:BFO from 1:9 to 5:5 and were subsequently ball-milled. The 10 MPa pressed CFO-BFO specimens were finally sintered at 820°C for 9h to obtain densified CFO-BFO composites.

Structure of composites was performed by means of X-ray diffraction using a D5005 diffractometer with $\text{CuK}\alpha$ radiation. The Raman scattering measurements were performed by T64000 Jobin – Yvon spectrometer using laser wavelength of 514 nm. The absorption spectra of composites were recorded by Jasco V670 photospectrometer using integral sphere in the wavelength band of 200 nm – 800 nm. Impedance spectra were obtained by a Le Croy ware Jet 332 equipment.

3. Result and discussion

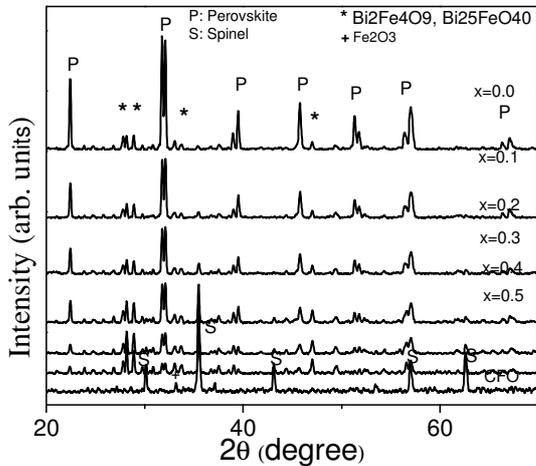


Figure 1: XRD patterns of (x) CoFe_2O_4 -(1-x) BiFeO_3 (x=0.0÷0.5) and CFO

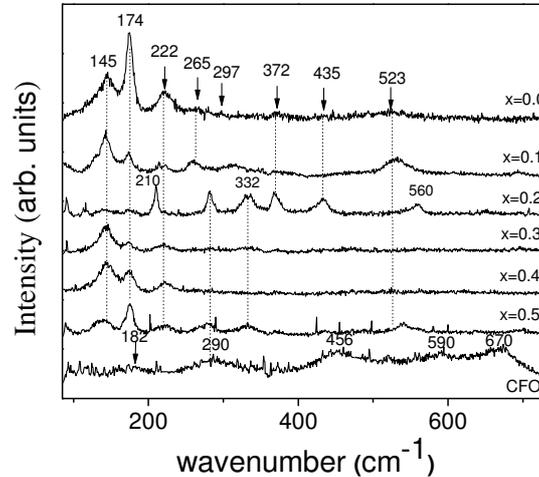


Figure 2: Raman spectra of (x) CoFe_2O_4 -(1-x) BiFeO_3 (x=0.0÷0.5) and CFO

Fig. 1 depicts the X-ray diffraction patterns of sintered (x)CFO-(1-x)BFO multiferroic composite powders with x=0, 0.1, 0.2, 0.3, 0.4, 0.5 and 1. It can be seen that the CFO-BFO_{x=0.1÷0.5} synthesized compounds exhibit a well polycrystallized phase which corresponds to a mix of perovskite phase (for BFO) and spinel phase (CFO). The spinel CFO phase belongs to $O_h^7(\text{Fd}\bar{3}m)$ space symmetric group with cubic inverse spinel structure. The perovskite BFO phase belongs to R_{3C} space symmetric group with hexagonal structure. Spinel material contains a small amount of Fe_2O_3 impurity and perovskite BFO material contains $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_{25}\text{FeO}_{40}$ impurity phases. These impurity phases exist in all composite samples, however, the intermediate phase between two component phases CFO and BFO is not occurred until x=0.5. Fig. 1 also shows that the intensity of peaks corresponding to the perovskite BFO phase decreases gradually whereas that of spinel CFO peaks increases gradually with increasing CFO concentration.

The vibration spectra of CFO-BFO composites were investigated by Raman scattering measurement and presented in Fig. 2. In the wave number range of 100 cm^{-1} ÷ 700 cm^{-1} , CFO phase contains five Raman peaks at 182, 290, 456, 590 and 670 cm^{-1} which corresponding to five Raman active modes A_g , E_g , $3 F_{2g}$ [12]. The modes at 590 and 670 cm^{-1} are related to the T-site mode that reflects the local lattice effect in the tetrahedral sublattice; other peaks at 182 cm^{-1} , 290 cm^{-1} and 456 cm^{-1} correspond to the O-site mode that reflects the local lattice effect in the octahedral sublattice. This relatively consists with report of Yuqiu [12]. BFO phase presents eight Raman peaks at 145, 174, 222, 265, 297, 372, 435 and 523 cm^{-1} which correspond to eight Raman active modes $4A_1(\text{LO})$ and $4E(\text{TO})$ [13]. The modes which are smaller than 300 cm^{-1} correspond to Bi-O vibrations while other peaks from 350 cm^{-1} to 600 cm^{-1} correspond to Fe-O vibrations.

It is known that the prepared samples are sintered composites thus there are simultaneous existence of two crystal particle kinds corresponding to CFO and BFO phases. For this reason, Raman spectra may depict the lattice vibrations that belong to one of two constitutive phases CFO and BFO, or even belong to the grain boundary region between two phases. Fig. 2 shows that almost the Raman peaks that belong to BFO component were exhibited in composite samples whereas those of CFO phase were not observed which may be due to their weak intensity. There is occurrence of some strange peaks located at 210 and 560 cm^{-1} in $x=0.2$ sample or at 332 cm^{-1} in $x=0.2$ and 0.5 samples. These peaks may be assigned to the lattice vibration in the grain boundary region between two phases.

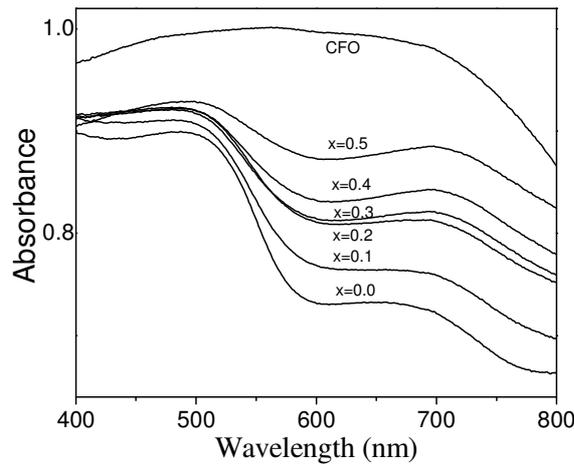


Figure 3: Absorption spectra of $(x)\text{CoFe}_2\text{O}_4-(1-x)\text{BiFeO}_3$

Fig. 3 shows the absorption spectra of CFO-BFO solid solutions. The calculated energy band gap of perovskite BFO phase is 2.14 eV corresponding to wave number of 579 nm . The optical band gap of these composites decreases slightly with the increase of CFO concentration. The energy band gaps are $2.14, 2.13, 2.11, 2.09, 2.07\text{ eV}$ corresponding to $x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5$. This proves the influence of CFO phase respect to BFO as mentioned in the Raman spectra analysis. We can see that the absorbance of composite in the wavelength range $550\text{ nm} \div 800\text{ nm}$ increases with CFO concentration which suggests the increase of conductance of composite. This can be explained as following, the simultaneous presence of Fe^{2+} and Fe^{3+} in CFO phase leads to electron hopping conduction from Fe^{2+} to Fe^{3+} . It is known that, the energy band gap of BFO created base on energy levels of $\text{Fe}^{3+}(3d)$ and $\text{O}^{2-}(2p)$ and the energy band gap of CFO is smaller than that of BFO, therefore the increase of CFO concentration leads to relatively high density of localized defect states in the energy band gap of BFO phase, the defect state is Fe^{2+} in this case, in which electron can hop from Fe^{2+} to not only neighboring Fe^{3+} of CFO but also to Fe^{3+} of BFO and CFO separated by different distance, may increase the conductance behaviour.

The room temperature magnetic properties of CFO-BFO composites can be obtained for the maximum magnetic field H_m of $13,500\text{ Oe}$ and showed in Fig. 4. It is clear that, the weak ferromagnetism is observed in $\text{CFO-BFO}_{x=0.0}$ instead of intrinsic antiferromagnetism of BFO. This was mentioned in P. Pandit research that room temperature ferromagnetism may exist in BFO if there is a continuing collapse of the space cycloidal spin structure [9].

Fig. 5 shows the relationship between the coercivity H_c or the squareness Mr/H_c of composites and CFO content. It is found that the coercivity H_c increases with the increase of CFO concentration in the composite. This result may arise from the magnetoelastic coupling [11] in which the coupling is dominated by elastic interaction in two phases CFO and BFO. The magnetoelastic coupling is caused by the magnetostriction of the CFO phase and the piezoelectricity of the BFO phase, due to the domain-wall motion and domain rotation of magnetic and electric domains. The slight increase in magnetic squareness Mr/H_c is observed when x increases from 0 to 0.3. However, CFO concentration about 30 mol% causes Mr/H_c to increase anomalously and reaches to the highest value of about 11.12 % with $x=0.4$, but decreases upon further increase of CFO concentration to 1.57 % with $x=0.5$. This reveals that, the optimal magnetic property in composite can be obtained with x of about 0.4.

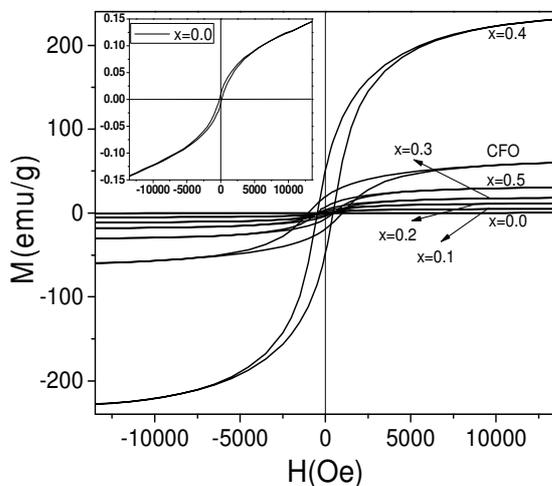


Figure 4: The M-H hysteresis loops of (x) $\text{CoFe}_2\text{O}_4-(1-x)\text{BiFeO}_3$

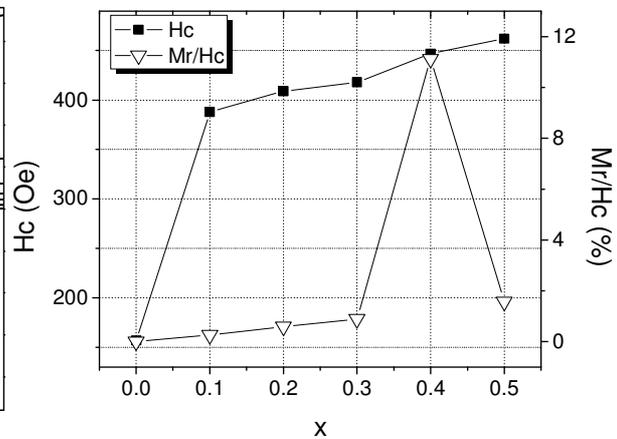


Figure 5: The coercivity H_c and squareness Mr/H_c of composites as a function of CFO

To elucidate the role of CFO on the conductivity, we have measured the impedance spectra of the samples. The impedance spectrum is usually used to characterize bulk grain, grain boundary and the electrode interface contributions by exhibiting successive semicircle Cole-Cole plots with its imaginary part plotted against its real part in the complex plane. A high frequency semicircle originates from the bulk conduction and the dielectric processes; a low frequency semicircle is associated with ion and electron transfers at the contact surface between the sample and the electrode, while an intermediate frequency semicircle contains the information on the grain boundary and impurity-phase impedance. Fig. 6 depicts the impedance spectra of CFO-BFO composite with different concentrations of CFO corresponding to $x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5$. In the case of CFO-BFO with $x=0.0$, the impedance contains two components which are grain and grain boundary impedance. In almost samples the contribution of the grain boundary impedance dominates so that we difficulty observe the grain semicircle in the samples CFO-BFO with $x=0.0\div 0.3$. However, the contribution of the grain impedance increases when CFO concentration reaches to 40%, therefore there are two semicircles in the impedance spectra of CFO-BFO composites with $x=0.4$ and 0.5 .

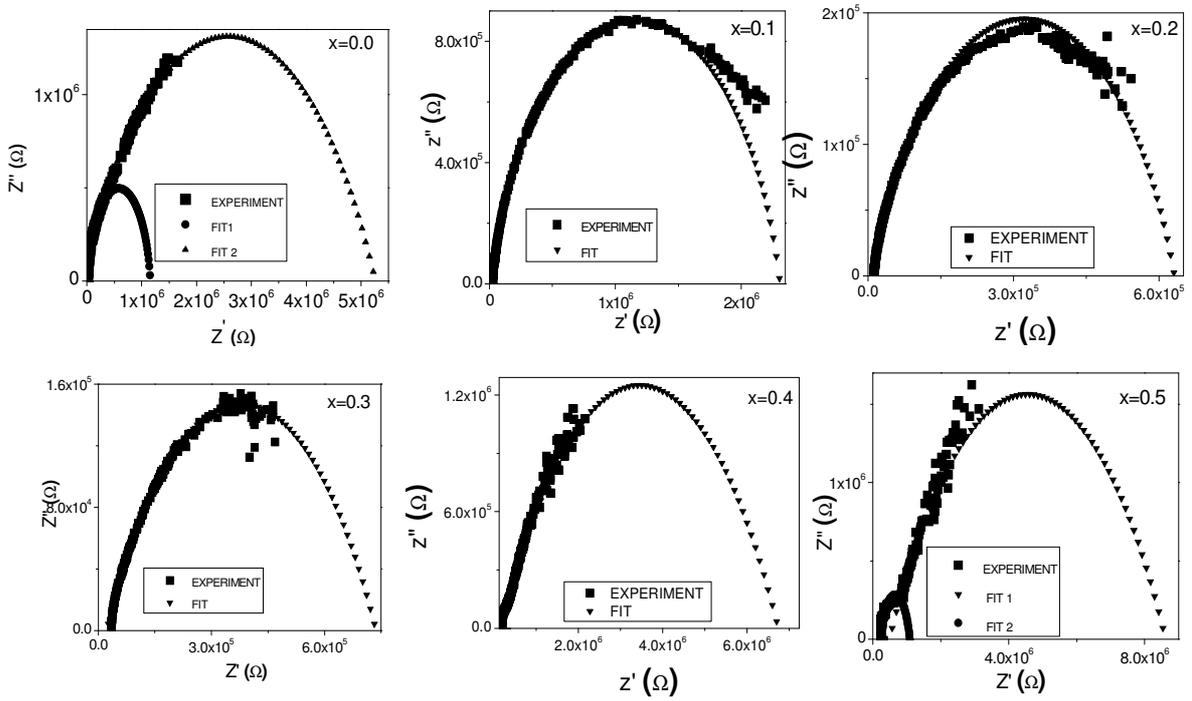


Figure 6: The impedance spectra of $(x)\text{CoFe}_2\text{O}_4-(1-x)\text{BiFeO}_3$

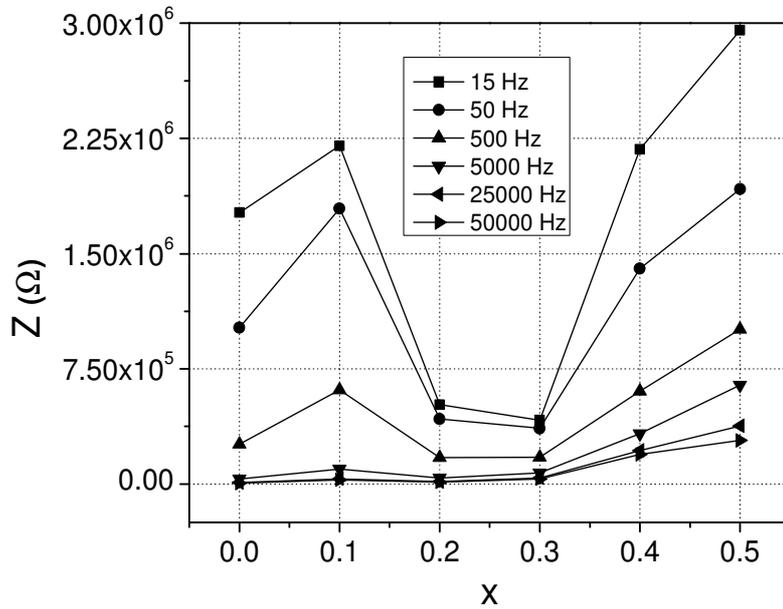


Figure 7: Impedance of composite as the function of CFO concentration at different frequencies

Fig. 7 shows the plots of impedance of composite as the function of CFO concentration at different frequencies. It is clear that the impedance of composite decreases when the CFO concentration ranges from 10% to 30%. However, it increases sharply when the CFO concentration is above 30%. To combine this result with that of M-H hysteresis loop analysis we can conclude that CFO-BFO_{x=0.4} composite not only has the largest ferromagnetism but also well maintains dielectric property.

4. Conclusion

The sintered (x)CoFe₂O₄-(1-x)BiFeO₃ (x=0.0÷0.5) spinel-perovskite composites have been well synthesized by two-step solid reaction technique. All samples exhibit a well polycrystallized phase that corresponds to a mix of two phases CFO and BFO and there is no intermediate phase between two component phases until x=0.5. The coercivity H_c and the squareness Mr/Hc as well as the impedance Z of composite samples have been found to vary with the CFO concentration. It has been shown that optimal magnetic properties, e.g. coercivity Hc and the squareness Mr/Hc, can be obtained with x of about 0.4. Moreover, the results of impedance measurements have indicated that the dielectric property of composite still be well maintained with x=0.4.

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