Journal of Alloys and Compounds 709 (2017) 158–164

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Measurement of temperature dependent magnetoelectricity in $BiFe_{(1-x)}Co_xO_3$; x = 0, 0.01, 0.02

S. Kuila, S. Tiwary, M.R. Sahoo, A. Barik, P.N. Vishwakarma*

Department of Physics and Astronomy, National Institute of Technology, Rourkela, Odisha 769008, India

ARTICLE INFO

Article history:
Received 2 February 2017
Received in revised form
9 March 2017
Accepted 10 March 2017
Available online 14 March 2017

Keywords:
Magnetoelectric measurement
Magnetoelectric coefficients
Magnetic disorder
Monoglass
Multiglass

ABSTRACT

A very handy setup is developed for the measurement of magnetoelectric (ME) voltage as a function of magnetic field and temperature. Using this setup, first and second order ME coupling coefficients of parent and cobalt substituted $BiFeO_3$ are obtained. Study of these ME coefficients suggests involvement of magnetic disorder can enhance the ME couplings by many folds. In the intrinsic region a nearly same value of the first order coefficient for all the three samples are found. The behavior of higher order coefficient shows that parent $BiFeO_3$ is of mono-glassy character whereas indications of multiglass nature is seen in the cobalt substituted $BiFeO_3$. This study suggests that, a very light substitution of Cobalt at the Fe site may leave the first order coefficients unperturbed but may initiate multiglassiness in the sample, which is highly desirable for enhancing the magnetoelectricity.

1. Introduction

Magnetoelectric multiferroics have been under focus of study for the last few years due to their futuristic device applications of unconventional nature [1–3]. Owing to their need-of-time applications, an understanding of the underlying physics leading to the coupling between the magnetic and the electric order parameter is immensely required. However, addressing such a trivial problem is not possible without a precise and convenient measurement technique. Some of the widely followed techniques are magneto-capacitance [4] or magnetodielectric, pyroelectric [5], magnetic field dependent polarization [6] and susceptibility measurements under electric fields [2]. Although having wide popularity, aforementioned techniques may pose certain limitations, for instance, the contribution of non-polar contributions to the magneto-dielectricity [7], polarization measurement involving measurement of leakage currents may be misleading in case of poor conducting samples and in the susceptibility measurements, it is difficult to apply electrical bias, while measuring magnetization using a VSM [8].

Another technique called "dynamic method" is relied by a large number of researchers, because of its simplicity and accuracy [9–11]. Here, a DC magnetic field is superimposed over a sinusoidal magnetic field and the induced magnetoelectric (ME) voltage is measured using a lock-in-amplifier. The sinusoidal nature of magnetic field does not allow charge accumulation at the electrodes [12]. However, due to the ac nature of magnetic field, an undesirable phase lag in the induced voltage with respect to the field is inevitable and thus a phase correction is of utmost importance [12]. Usually ME effect is described only by the linear ME coefficient (α) as it is the dominant coupling term [13]. Using dynamic method, apart from α, one may also obtain the quadratic term β, and other higher order terms [14].

One of the magnetoelectric compound which has drawn considerable attention of the researchers is $BiFeO_3$ (antiferromagnetic $T_N \sim 643\,K$, ferroelectric $T_c \sim 1103\,K$) [15]. As both the ordering temperatures are much above the room temperature, this compound is believed to be an ideal case for the investigation of magnetoelectricity, which arises due to coupling between the electric and magnetic ordering parameters. The evidence of magnetoelectric coupling in bulk $BiFeO_3$ has been reported via various studies such as Raman-scattering [16], neutron-scattering [17,18], terahertz spectroscopy [19], etc. Besides these indirect methods, direct measurements of magnetoelectricity on $BiFeO_3$ have also been reported by several authors [20–23]. However, the measurement frequencies adopted were too high from the point of view of phase correction and electrical conductivity. Hence a low

* Corresponding author.
E-mail addresses: prakashn@nitrkl.ac.in, pnviisc@gmail.com (P.N. Vishwakarma).

http://dx.doi.org/10.1016/j.jallcom.2017.03.118
0925-8388/

frequency measurement is very much desirable.

The origin of magnetoelectric coupling in $BiFeO_3$ has been attributed to be the combined effect of magnetostriction [24] and inverse Dzyaloshinski-Moriya (DM) effect [25]. In a size reduced nano-$BiFeO_3$, where the spin cycloid arrangement is disrupted, the contribution of inverse DM effect is expected to be suppressed, so that the ME coefficients are dominated by the magnetostriction. Disruption in the magnetic cycloid may also be evidenced from the linear behavior of ME coefficient in nano-$BiFeO_3$, which otherwise is quadratic in bulk $BiFeO_3$ [26]. However, size reduction also leads to the occurrence of spin-glass phenomena, which is absent in bulk $BiFeO_3$ [26]. Thus, in nano-BFO, this spin glass phenomenon may act as additional parameter and its effect on the ME coupling must be examined critically.

Recently there have been several reports of ME coupling in glassy magnetoelectrics and multiglass (magnetically as well as electrically disordered) systems [27–31]. It has been found that higher order magnetoelectric effects are dominated in disordered multiferroics [32,33]. The disordered array of magnetic cations are also found to display relaxor-type ferroelectricity (with polarization values as high as 1.3 μC m^{-2} at 5 K) in $CuFe_{0.5}V_{0.5}O_2$ [34]. In an earlier report, the cobalt substituted $BiFeO_3$ are also found to exhibit relaxor-type dielectric behavior below Neel temperature [35]. It thus seems that besides the ordering parameters, the disorder parameter may have an important role to play in the establishment of ME couplings. As the nanoparticles of $BiFe(Co)O_3$, have been found to exhibit spin-glass disorder, effect of the same must be examined in the displayed magnetoelectricity.

2. Experimental details

The $BiFe_{1-x}Co_xO_3$: x = 0 (BFO), x = 0.01 (BFCO1) and x = 0.02 (BFCO2) are prepared via sol–gel auto-combustion route as described in ref.36. The higher value of ‘x’ is not attempted, because it was reported by J.Ray et al. that, substitution above x = 0.02 results in the appearance of secondary phase [37].

Magnetoelectric (ME) measurements are carried out adopting the dynamic method [38]. A schematic diagram is shown in Fig. 1. Our magnetoelectric measurement setup makes use of a Helmholtz coil (diameter 8 mm) having 125 turns of winding on each side with separation of 4 mm. The measured resistance and inductance of the Helmholtz coil are 8Ω and 240 μH respectively. The sample (in pellet form) is mounted on a mica sheet and inserted between the coils. Being a decent thermal conductor, but a bad electrical conductor, mica sheet is used so that the sample, thermometer and heater coil are thermally connected to each other. The temperature of the sample is measured using a Pt-100 thermometer, mounted adjacent to the sample. A heater wire (Manganin) of resistance 40Ω is wound over the mica-sheet to vary and control the temperature of the sample. The sample sticking to the mica sheet is inserted vertically between the coils such that the sample is placed in the middle of the Helmholtz coil and the direction of the sample surface is parallel to the magnetic field. This setup is put inside a glass tube and evacuated. For lowering the temperature, the glass tube is dipped in liquid nitrogen. While measurement, the coil assembly is placed between the poles of DC electromagnet, whose field may be varied from +10 kOe to −10 kOe, using a bipolar power supply. The DC magnetic field (H) is measured using LakeShore 425 Gaussmeter. The glass tube between the pole pieces is kept in such a way that the magnetic field lines of Helmholtz coil are along the DC magnetic field lines. Use of conducting silver paste epoxy is made to electrically connect the sample to the measuring probes. Coaxial wires are used to supply AC signal to Helmholtz coil as well as to measure the induced ME voltage.

The sample is excited by an AC magnetic field, $h = h_0 \sin \omega t$, where $h_0 = 20$ Oe and $\omega = 2\pi f$, f is driving frequency. AC signal is applied to the Helmholtz coil using internal oscillator of lock-in-amplifier (SR 830) and the induced magnetoelectric voltage (V) is measured using the same the lock-in-amplifier. The temperature is recorded using temperature controller (LakeShore 331). The data

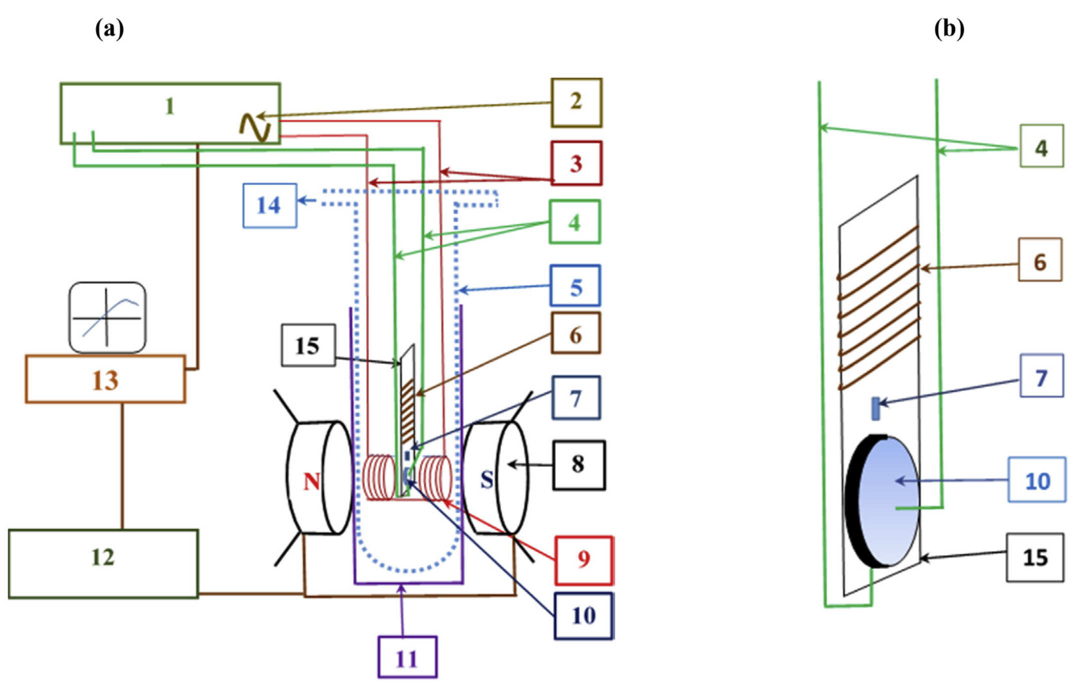

Fig. 1. (a) - Schematic diagram of actual setup for temperature dependent magnetoelectric measurement: 1. Lock-in Amplifier (LIA), 2. Internal oscillator of LIA, 3. AC signal probe, 4. ME voltage measuring probe, 5. Glass tube, 6. Heater coil, 7. Pt-100 sensor, 8. DC electromagnet, 9. Helmholtz coils, 10. Sample, 11. Liquid N_2 container, 12. DC magnet power supply, 13. Computer Interface, 14. Vacuum pipe, 15. Mica sheet. (b)- Expanded view of sample mounting portion.