Feeble ferromagnetism and double relaxation mechanism in Bi$_{0.42}$Ho$_{0.28}$Ba$_{0.24}$Ca$_{0.06}$Fe$_{0.7}$Ti$_{0.3}$O$_3$ ceramics

Chiranjib Chakrabarti$^{a}$, Songliu Yuan$^{a}$, Qingshan Fu$^a$, and Anirban Das$^{b}$

$^a$ School of Physics, Huazhong University of Science and Technology, Wuhan 430074, People’s Republic of China
$^b$ Department of physical and material Sciences, College of engineering and management, Kolaghat, Purba Medinipur, West Bengal 721171, India

e-mail: yuansl@hust.edu.cn (Songliu Yuan)
anirban_das@cemk.ac.in (Anirban Das)
chiranjib1987@yahoo.com (Chiranjib Chakrabarti)

Abstract. The structural, magnetic, and dielectric studies on Bi$_{0.42}$Ho$_{0.28}$Ba$_{0.24}$Ca$_{0.06}$Fe$_{0.7}$Ti$_{0.3}$O$_3$ ceramics present some exciting outcomes. An XRD based structural study shows that the ceramics hold an ABO$_3$-type perovskite network. Room-temperature MH-hysteresis study detected the trace of ferromagnetism in the ceramics. The temperature-dependent dielectric study exhibits that a double relaxation mechanism is engaged for a wide range of temperature and frequency.

1. Introduction

Recently, BiFeO$_3$ has emerged as a novel material to the researchers because of its excellent multiferroic properties at room temperature that exhibits numerous commercial application possibilities in spintronics, memory elements, sensors, actuators, etc.[9] Unfortunately, some stumbling blocks, such as poor magnetic properties and defect-related conductions, creates a severe challenge for the application possibilities of this class of material.[5, 7] A substantial amount of effort was made to overcome this problem, such as the substitution of A- with Rare earth or B-site sites with a transition metal or creating binary or trinary networks with other suitable perovskite materials.[1, 7]. In our previous work,[5] the presence of Ho-holding a perovskite-ferrite form is demonstrated in a series of BFO based solid-solutions. Here, the phase-structural, magnetic, and dielectric studies on Bi$_{0.42}$Ho$_{0.28}$Ba$_{0.24}$Ca$_{0.06}$Fe$_{0.7}$Ti$_{0.3}$O$_3$ ceramics are discussed, and possible relaxation mechanism in this material is portrayed.

2. Synthesis and characterizations

Polycrystalline samples of Bi$_{0.42}$Ho$_{0.28}$Ba$_{0.24}$Ca$_{0.06}$Fe$_{0.7}$Ti$_{0.3}$O$_3$ were prepared by a solid-state reaction process. The details of the preparation procedure are elaborated elsewhere. [5] The phase structural analysis of the sample was performed by an X-ray powder diffractometer (Model no: MXP18AHF, MARK, Japan). The temperature dielectric properties at different frequencies were investigated using a precision impedance analyzer (Model no: Wayne Kerr 6500B).

3. Results and discussions

Fig. 1(a) shows the refined X-ray diffraction pattern (XRD) of Bi$_{0.42}$Ho$_{0.28}$Ba$_{0.24}$Ca$_{0.06}$Fe$_{0.7}$Ti$_{0.3}$O$_3$ ceramics at room temperature. The crystalline phases and structural parameters of Bi$_{0.42}$Ho$_{0.28}$Ba$_{0.24}$Ca$_{0.06}$Fe$_{0.7}$Ti$_{0.3}$O$_3$ were obtained from XRD pattern analysis followed by a Reitveld refinement using X’pert refinement using X’pert pro and Full prof software, respectively. The phase analysis indicated the existence of $R3c$ (~23.2%), $P4mm$ (~60.6%),

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and *Pbnm* (~16.2%) phase in the ceramics network, which identifies the presence of BiFeO₃, BaTiO₃, and HoFeO₃, respectively. Therefore the ceramic network contains a complete perovskite structure. Moreover, the Rietveld refinement result exhibits an excellent $\chi^2$ value (~1.8) with reliability factors: $R_p=48.5$ and $R_{wp}=31.3$.

![Refined X-Ray Diffraction patterns measured at room temperature](image)

As shown in Fig. 1(b), the room temperature magnetization-magnetic field hysteresis (M-H) in the Bi$_{0.42}$Ho$_{0.28}$Ba$_{0.24}$Ca$_{0.06}$Fe$_{0.7}$Ti$_{0.3}$O$_3$ sample indicating a ferromagnetic behavior. The enlarged part of the hysteresis curve estimates the $M_r$ (0.075 emu g$^{-1}$) and $H_c$ (~0.0601 kOe) value of the sample. The obtained $M_r$ value is comparable to the previously reported 0.7BiFeO$_3$-0.3Ba$_{0.75}$Ca$_{0.25}$TiO$_3$ (~0.07 emu g$^{-1}$) ceramics[3] and considerably improved than that in the BSFO (~0.0017 emu g$^{-1}$) ceramics.[2] Such origin of the weak ferromagnetism in the Bi$_{0.42}$Ho$_{0.28}$Ba$_{0.24}$Ca$_{0.06}$Fe$_{0.7}$Ti$_{0.3}$O$_3$ sample can be attributed to the combination of two different mechanisms (1) ferromagnetic exchange interaction between Fe and Ho ions, and (2) canting mechanism in Fe$^{3+}$ spins due to the substitution.[5, 6]

The temperature-dependent relative permittivity in Bi$_{0.42}$Ho$_{0.28}$Ba$_{0.24}$Ca$_{0.06}$Fe$_{0.7}$Ti$_{0.3}$O$_3$ ceramics under a wide range of frequencies (10kHz-1MHz) are shown in Fig. 2(a). Careful observation reveals that two different anomalies are present; one at a lower temperature region (~407 K) and the other one at a relatively higher temperature region (~ 600 K), namely A₁ and A₂ regions, respectively. Such dual anomalous behavior also can be observed in the temperature variation of the $\tan \delta$ curve (inset of Fig. 2(a)). A similar anomalous response was previously observed in (1-$x$) BiFeO$_3$-$x$(0.5CaTiO$_3$-0.5SmFeO$_3$) ceramics, which was attributed to the different relaxation processes in the ceramics.[8] It was demonstrated that A₂ is probably due to the grain boundary effect, and A₁ is related to the charge ordering in mechanism between the Fe ions.
Fig. 2(b) presents the temperature-dependent AC conductivity ($\sigma_{AC}$) measurement in Bi$_{0.42}$Ho$_{0.28}$Ba$_{0.24}$Ca$_{0.06}$Fe$_{0.7}$Ti$_{0.3}$O$_3$ sample, which is obtained from the following relationship:[4]

$$\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon_r \tan \delta$$

(1)

Besides, the change of slopes, as indicated by the arrows, indicates different relaxation mechanism is active inside the material. Therefore, the entire temperature range is divided into three regions: (i) The frequency-independent high-temperature region I, where $\sigma_{AC}$ increases sharply, partially frequency-dependent region II, where the defect conductivity is a crucial factor for conduction process, and (iii) a frequency-dependent low-temperature region III, $\sigma_{AC}$ is nearly constant over the frequency range. In this region, the relaxation mechanism is attributed to the carrier hopping.[4] Interesting that, the slope of the curve primarily changes at two junction points, which can be recognized as $A_2$ and $A_1$ at lower and higher temperature region, respectively. Hence, the anomaly at $A_1$ can be identified as the charge ordering due to the carrier hopping between Fe$^{2+}$-Fe$^{3+}$ in the perovskite network, while the anomaly at $A_2$ is probably due to the grain boundary defect based conductivity, such as Bismuth or oxygen vacancy triggered conduction mechanism.

Fig. 2 Temperature-dependent relative permittivity (a) and tangent loss (inset) under different frequencies in Bi$_{0.42}$Ho$_{0.28}$Ba$_{0.24}$Ca$_{0.06}$Fe$_{0.7}$Ti$_{0.3}$O$_3$ ceramics. Variation of A.C conductivity with 1000/T (b) in the same ceramics.

4. Conclusion

The phase-structural, room-temperature magnetic, and temperature-dependent dielectric studies are performed for the Bi$_{0.42}$Ho$_{0.28}$Ba$_{0.24}$Ca$_{0.06}$Fe$_{0.7}$Ti$_{0.3}$O$_3$ ceramics. XRD analysis, along with Rietveld refinement, indicated that the ceramic holds a perovskite network containing three different (ABO$_3$) perovskites. Room-temperature MH-hysteresis study indicated weak ferromagnetism in the sample. Besides, a detailed high-temperature dielectric analysis revealed that two different relaxation mechanisms exist in the sample, the one at a relatively lower temperature occurs from the carrier hopping and the other
one, at a relatively higher temperature, emerges from the Bismuth or oxygen vacancy related defects inside the crystal.

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Nomenclature

\[ \sigma_{AC} \quad \text{AC conductivity (S m}^{-1}) \]

\[ f \quad \text{frequency of ac current (Hz)} \]

\[ \tan \delta \quad \text{tangent loss} \]

\[ \varepsilon_0 \quad \text{absolute permittivity} \]

\[ \varepsilon_r \quad \text{relative permittivity} \]