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Magnetic and dielectric properties of Aurivillius phase $\text{Bi}_{4.2}\text{Nd}_{0.8}\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$

J. YANG^{1(a)}, L. H. YIN¹, D. F. SHAO¹, X. B. ZHU¹, J. M. DAI¹ and Y. P. SUN^{1,2(b)}

¹ Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences
Hefei 230031, PRC

² High Magnetic Field Laboratory, Chinese Academy of Sciences - Hefei 230031, PRC

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Abstract – The magnetic and dielectric properties of $\text{Bi}_{4.2}\text{Nd}_{0.8}\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$ are investigated by using the measurements of magnetization and dielectric constant. The sample is ferromagnetic with the Curie temperature of 428 K. And the remnant magnetization M_r is 0.5 emu/g, which is two orders of magnitude higher than M_r of $\text{Bi}_5\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$. The ferromagnetism in $\text{Bi}_{4.2}\text{Nd}_{0.8}\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$ can be ascribed to spin canting of the Fe-based and Co-based sublattices via Dzyaloshinskii-Moriya interaction. Both the dielectric constant and dielectric loss have the characteristics of relaxation, and the activation energy turns out to be 0.658 ± 0.013 eV.

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The bismuth-based layer-structured compounds with the formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$ ($\text{A} = \text{Na}, \text{K}, \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}, \text{Bi}$, etc., and $\text{B} = \text{Ti}, \text{Fe}$, etc.) have attracted much attention because of the potential candidates as single-phase multiferroics by doping magnetic species at the B-site into ferroelectric matrices [1,2]. The Aurivillius compounds are built from intergrowths of $(\text{Bi}_2\text{O}_2)^{2+}$ and perovskite-like layer $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$, where n denotes the number of sheets of corner-sharing BO_6 octahedral forming the perovskite blocks [3]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($n=3$) as a prototype of Aurivillius phase was previously studied for nonvolatile memory because of large spontaneous polarization and high ferroelectric Curie temperature arising from lone pair electrons inside Bi^{3+} ions [4,5]. By inserting BiFeO_3 into $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, a typical $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ ($n=4$) phase with a four-layered structure can be formed [6]. Its magnetoelectric properties were studied recently and the observed magnetization is actually small at room temperature [7,8]. Huang *et al.* realized a weak ferromagnetism (FM) at room temperature in $\text{Bi}_{4.15}\text{Nd}_{0.85}\text{FeTi}_3\text{O}_{15}$ [9]. Mao *et al.* found that the Co-substituted for the Fe compound $\text{Bi}_5\text{Fe}_{0.5}\text{Co}_{0.5}\text{Ti}_3\text{O}_{15}$ presents an enhanced FM with the remnant magnetization

(M_r) 0.0039 emu/g at room temperature, and proposed that the FM in $\text{Bi}_5\text{Fe}_{0.5}\text{Co}_{0.5}\text{Ti}_3\text{O}_{15}$ may originate from the coupling between $\text{Fe}^{3+}\text{-O-Co}^{3+}$ octahedral clusters [1]. However, the $\text{Fe}^{3+}\text{-O-Co}^{3+}$ will favor the formation of antiferromagnetic (AFM) superexchange interactions according to Goodenough-Kanamori rules [10,11]. In order to shed light on understanding the nature of the FM in the $n=4$ Aurivillius compounds, we investigated $\text{Bi}_{4.2}\text{Nd}_{0.8}\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$ by using the measurements of magnetization, dielectric constant, and ferroelectric hysteresis.

Polycrystalline $\text{Bi}_{4.2}\text{Nd}_{0.8}\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$ was prepared by a conventional solid state reaction. The starting materials Bi_2O_3 (99.9%), Nd_2O_3 (99.9%), Fe_2O_3 (99.8%), TiO_2 (99.9%), and Co_2O_3 (99%) were weighted in the stoichiometric ratio, and then mixed thoroughly and pressed into pellets. They were sealed in an evacuated quartz tube and then pre-fired at 600 °C for 20 h. The pellets obtained were ground, pelletized, sealed, and sintered at 800 °C for 20 h with two intermediate grindings, and finally, the furnace was cooled down to room temperature. The crystal structure was examined by X-ray diffractometer using $\text{Cu } K\alpha$ radiation at room temperature (RT). The microstructure was characterized by a Sirion 200 field emission scanning electron microscopy (SEM) from FEI company. The temperature

^(a)E-mail: jyang@issp.ac.cn

^(b)E-mail: ypsun@issp.ac.cn

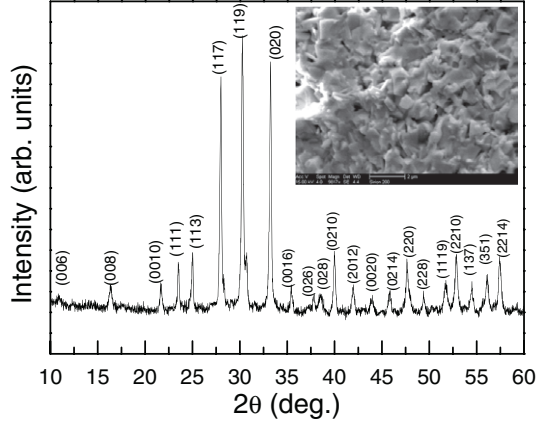


Fig. 1: XRD patterns of BNTFCO at RT. The inset shows SEM image.

dependence of magnetization was carried out from RT to 800 K using a Physical Property Measurement System-vibrating sample magnetometer (PPMS-VSM) with a high-temperature oven option. The magnetization hysteresis measurements were performed with a Quantum Design superconducting quantum interference device (SQUID) MPMS system ($2 \leq T \leq 400$ K, $0 \leq H \leq 5$ T). Dielectric measurements were performed using an LCR meter in the frequency range 1k–1MHz at temperatures ranging from RT to 750 K. RT FE hysteresis loops were measured by using a TF Analyzer 2000 (aixACCT) at a frequency of 10 Hz. For the sake of description, the sample $\text{Bi}_{4.2}\text{Nd}_{0.8}\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$ is labeled as BNTFCO.

Figure 1 shows the powder XRD pattern and SEM image at RT. The results reveal that the sample is single phase with no detectable secondary phases and the XRD pattern can be indexed by an orthorhombic lattice with the space group $A21am$ (No. 36), which is consistent with the previous results [12]. Figure 2(a) shows the temperature dependence of magnetization in the zero-field-cooled (ZFC) and the field-cooled (FC) modes in the temperature range 300–600 K at an applied field of 100 Oe for BNTFCO. It is found that there is a deviation between the ZFC magnetization (M_{ZFC}) and the FC magnetization (M_{FC}) curves below 425 K. The sample seems to undergo a PM-to-FM magnetic transition at 428 K (defined as the temperature corresponding to the peak of dM/dT , as shown in the inset of fig. 2(a)). Moreover, the M_{ZFC} exhibits a cusp at the temperature of 412 K. The experimental features regarding the typical irreversibility found in M_{FC} and M_{ZFC} with a cusp in the plot of M_{ZFC} as well as the non-saturation of the FC magnetization at temperatures far below T_C are reminiscent of cluster glasses. The temperature dependence of inverse magnetic susceptibility χ_m ($1/\chi_m = H/M$) of BNTFCO is shown in fig. 2(b). For a ferromagnet in the PM region, the relation between χ_m and temperature T should follow the Curie-Weiss law, *i.e.*, $\chi_m = C_m/(T - \theta_p)$, where C_m is the molar Curie constant, and θ_p is the paramagnetic Curie temperature.

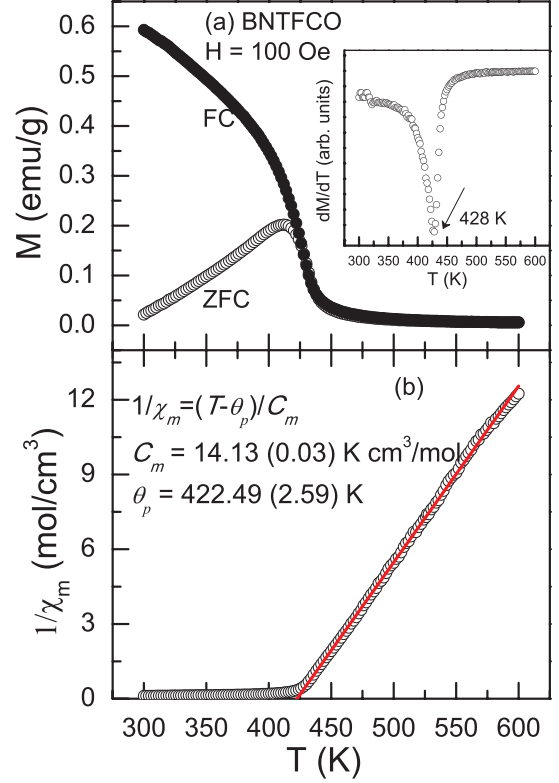


Fig. 2: (Colour on-line) (a) Magnetization of BNTFCO as a function of temperature in the ZFC and FC modes measured at $H = 100$ Oe. The inset is the plot of dM/dT . (b) Temperature dependence of the inverse susceptibility for BNTFCO. The solid line denotes the fit based on the Curie-Weiss law.

The line is the calculated curve deduced from the Curie-Weiss equation. It is found that the experimental curve in the whole PM temperature range can be well described by the Curie-Weiss law. The paramagnetic Curie temperature θ_p is obtained to be 422.49 ± 2.59 K, which almost coincides with the value of T_C . The Curie constant C_m deduced from the fitting data is 14.13 ± 0.03 K cm³/mol for BNTFCO. Thus, the effective magnetic moment can be determined to be μ_{eff} of $5.319 \pm 0.006 \mu_B$. In a mean field approximation, for one type of magnetic ions, the expected paramagnetic effective moment μ_{eff} is given by $\mu_{eff}^2 = xg^2S(S+1)\mu_B^2$, where x is the fraction of magnetic ions per formula unit, g the gyromagnetic factor, and S their spin quantum number. As a result, the expected effective moment μ_{eff} of BNTFCO can be obtained as $\mu_{eff} = 5.43 \mu_B$. It can be seen that the expected effective moment ($5.43 \mu_B$) is in agreement with the experimental data ($5.319 \pm 0.006 \mu_B$) implying that both Fe^{3+} and Co^{3+} contribute to the magnetization of BNTFCO.

In order to make the nature of magnetic structure of BNTFCO clear, we performed the magnetic hysteresis measurements at 5 and 300 K, as shown in fig. 3(a). The magnetization at 5 K exhibits a large hysteresis loop with a coercive field H_c of 3.1 kOe and remnant magnetization M_r of 2.42 emu/g. In addition, the magnetization does

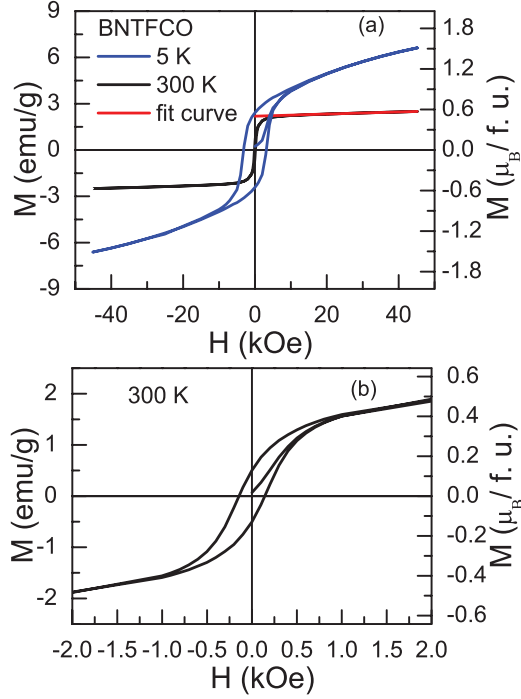


Fig. 3: (Colour on-line) (a) M vs. H at the temperature of 5 and 300 K. The solid line denotes a linear extrapolation of $M(H)$ to $H = 0$ at 300 K. (b) Magnetization hysteresis loop of BNTFCO in the low-field region at 300 K.

not saturate even at higher fields, revealing a superposition of both FM and AFM components. The M - H plot at 300 K shows a different behavior compared to that at 5 K. A small hysteresis loop can be observed (fig. 3(b)) with a coercive field H_c of 150 Oe and remnant magnetization M_r of 0.5 emu/g. The value of M_r of BNTFCO is 128 times larger than that of $\text{Bi}_5\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$ (3.9×10^{-3} emu/g) (ref. [1]) and is five orders of magnitude larger than that of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ (1.35×10^{-6} emu/g) (ref. [13]). Moreover, it is found that the rapid increase of magnetization at low magnetic fields resembles a ferromagnet with a long-range FM ordering corresponding to the rotation of magnetic domains, whereas the magnetization M increases continuously and slowly and does not saturate at higher fields, implying the appearance of a small amount of AFM phase. The coexistence and competition between FM and AFM interaction would favor the formation of a cluster glass state, which is consistent with the results shown in fig. 2(a). A linear extrapolation of $M(H)$ to $H = 0$ at 300 K allows us to determine the spontaneous magnetization μ_s as $0.56 \mu_B$ /f.u. This value is much smaller than the mean spin-only value of isolated Fe^{3+} ($2.5 \mu_B$) and Co^{3+} ($2 \mu_B$) ions implying that the FM did not originate from the Fe or Co clusters but from the interaction between Fe^{3+} and Co^{3+} via the medium of oxygen. It is noted that this value ($0.56 \mu_B$) almost corresponds to the expected value ($0.5 \mu_B$) for a collinear AFM alignment of magnetic moments of Fe^{3+}

and Co^{3+} ions through the Fe^{3+} -O- Co^{3+} superexchange interactions. However, the absence of a key feature, *i.e.* hyperbola behavior in the plot of $1/\chi_m$ vs. T implies that the ferromagnetism in BNTFCO does not arise from the ferrimagnetic coupling of Fe^{3+} -O- Co^{3+} . Mao *et al.* ascribed the ferromagnetism above room temperature in $\text{Bi}_5\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$ to the FM coupling of Fe-O-Co octahedral clusters [1]. It is expected that if the occupancy of Fe^{3+} and Co^{3+} ions in BNTFCO is 1:1 ordered, the exchange interaction between the high-spin state of Fe^{3+} and Co^{3+} would be the nature of AFM coupling according to Goodenough-Kanamori rules and thus BNTFCO would exhibit a typical ferrimagnetic ground state due to the differences in the magnetic moment of Fe and Co ions. However, it was proposed that Fe ions can occupy two non-equivalent positions in the four perovskite-like layers between the $(\text{Bi}_2\text{O}_2)^{2+}$ layers and the occupancy of Fe ions in $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ is random with Ti ions. Analogically, the occupancy of Co ions also distributed randomly at Ti sites in the sample BNTFCO. It is expected that there is Fe^{3+} -O- Fe^{3+} , Co^{3+} -O- Co^{3+} and Fe^{3+} -O- Co^{3+} interactions present in BNTFCO. Since the sample contains equal proportion of Fe and Co ions, one would expect a dominant Fe^{3+} -O- Co^{3+} interaction. Taking into account of the distorted crystal structure with tilted $\text{Fe}(\text{Co})\text{O}_6$ octahedra giving rise to canted spin structures, the observed ferromagnetism in BNTFCO is proposed to originate from spin canting of the Fe-based and Co-based sublattices via Dzyaloshinsky-Moriya interaction (refs. [14,15]) due to the octahedral tilting between the adjacent Co-O and Fe-O octahedra. The substitution of Nd for Bi ions will make $\text{Fe}(\text{Co})\text{O}_6$ octahedra more distorted, which facilitate those spins opposite to the field to align towards the applied field resulting in the enhanced magnetization of BNTFCO compared to BTFCO.

Figures 4(a) and (b) show the temperature dependence of the dielectric constant ϵ' and the dielectric loss $\tan\delta$ at different frequencies from RT to 750 K, respectively. A remarkable feature in the ϵ' - T curve is the anomaly in the vicinity of the FM transition temperature T_C . The dielectric constant decreases steeply below T_C , which suggests that the magnetic ordering suppresses the dielectric constant. A similar cusp of ϵ' - T curves correlated with the magnetic ordering can be observed in some ferroelectric antiferromagnets such as hexagonal rare-earth manganites [16]. The dielectric constant decreases with increasing frequency, which is a normal behavior of ferroelectrics. Moreover, the dielectric loss peak is observed around T_C and it normally appears at the temperatures at which the dielectric constant varies remarkably. It is noted that the position of the peak shifts toward a higher temperature with increasing temperature. Actually, the strong frequency dispersion of ϵ' and the frequency dependence of the loss peak are characteristics of relaxor ferroelectric and this dielectric relaxation may be ascribed to a thermally activated process. If so, the characteristic relaxation frequency f_r (peak in the dielectric loss spectra)

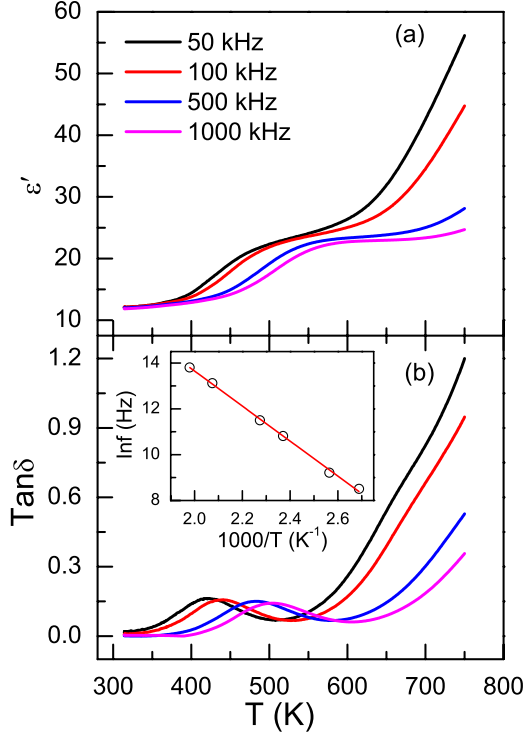


Fig. 4: (Colour on-line) (a) Temperature dependence of dielectric constant of BNTFCO at the frequency of 50, 100, 500, and 1000 kHz. (b) Temperature dependence of the dielectric loss at the frequency of 50, 100, 500, and 1000 kHz. The inset shows the Arrhenius plot of relaxation frequency *vs.* temperature.

should obey the Arrhenius law: $f_r = f_\infty \exp(-E_a/k_B T)$, where f_∞ is the relaxation frequency at infinite temperature and E_a is the activation energy, k_B is the Boltzmann constant, and T is the temperature. From the inset of fig. 4(b), a linear relation between $\ln f_r$ and the inverse of peak temperature manifests that the relaxation process can be well described by the Arrhenius law and thus the relaxation parameters f_∞ and E_a can be obtained as $(3.89 \pm 1.37) \times 10^{12}$ Hz and 0.658 ± 0.013 eV, respectively. This value of activation energy is comparable to that in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (0.87 eV) (ref. [17]) and Bi:SrTiO_3 solid solutions (0.74–0.86 eV) (ref. [18]).

In order to make the nature of the relaxation process clear, we performed the measurements of the frequency dependence of the real and imaginary parts of the complex dielectric constant, as shown in figs. 5(a) and (b), respectively. According to the Cole-Cole relation [19], the real and imaginary parts of the complex dielectric constant as a function of frequency are given by

$$\epsilon' = \epsilon_\infty + \frac{(\epsilon_s - \epsilon_\infty)[1 + (\omega\tau_0)^{1-\alpha} \sin 0.5\alpha\pi]}{1 + 2(\omega\tau_0)^{1-\alpha} \sin 0.5\alpha\pi + (\omega\tau_0)^{2(1-\alpha)}}, \quad (1)$$

$$\epsilon'' = \frac{(\epsilon_s - \epsilon_\infty)(\omega\tau_0)^{1-\alpha} \cos 0.5\alpha\pi}{1 + 2(\omega\tau_0)^{1-\alpha} \sin 0.5\alpha\pi + (\omega\tau_0)^{2(1-\alpha)}}, \quad (2)$$

where ϵ_s is the static dielectric constant, ϵ_∞ is the dielectric constant at high frequency, $(\epsilon_s - \epsilon_\infty)$ is the dielectric

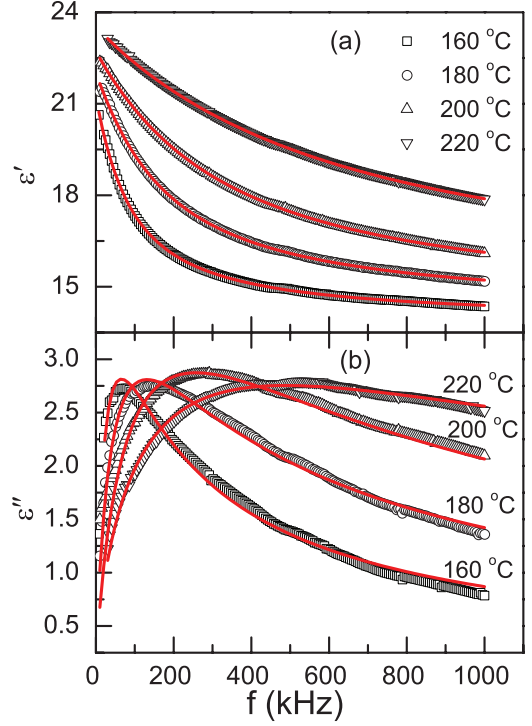


Fig. 5: (Colour on-line) Frequency dependence of (a) the real part, and (b) imaginary part of the complex dielectric constant of BNTFCO at the temperature of 160, 180, 200, and 220 °C. The solid lines denote the best fit to the experimental data according to eq. (1) and (2).

relaxation strength, $\omega = 2\pi f$ is the angular frequency, τ_0 is the relaxation time, and α is the broadening factor, which varies from 0 to 1 ($\alpha = 0$ for an ideal Debye relaxation). It is found that the fitting results according to eqs. (1) and (2) are well matched with the experimental data as shown in fig. 5. Moreover, the real and imaginary parts of the complex dielectric constants exhibit one relaxation process with a single relaxation time. If the additional contributions to the relaxation process, *e.g.* grain boundary, account for the relaxation process, the experimental data should include one more characteristic relaxation time, as shown in $\text{Sr}_2\text{SbMnO}_6$ [20]. Therefore, the dielectric relaxation process is associated with the grains of $\text{Bi}_{4.2}\text{Nd}_{0.8}\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$.

In summary, we have studied the magnetic and dielectric properties of Aurivillius phase $\text{Bi}_{4.2}\text{Nd}_{0.8}\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$. The sample exhibits an enhanced ferromagnetism and a weak ferroelectricity at room temperature with M_r of 0.5 emu/g, which is 128 times larger than M_r of $\text{Bi}_5\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$ (3.9×10^{-3} emu/g). The observed ferromagnetism in $\text{Bi}_{4.2}\text{Nd}_{0.8}\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$ is proposed to originate from spin canting of the Fe-based and Co-based sublattices via Dzyaloshinskii-Moriya interaction due to the octahedral tilting between the adjacent Co-O and Fe-O octahedra. The dielectric loss peak is observed around T_C , and the activation energy is determined to be 0.658 ± 0.013 eV. Moreover, the

dielectric relaxation process is originating from the grains of $\text{Bi}_{4.2}\text{Nd}_{0.8}\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$.

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