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Magnetic and phonon transitions in B-site Co doped BiFeO₃ ceramics

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Abstract

Magnetic susceptibility and phonons have been characterized in multiferroic Bi(Fe_{1-x}Co_x)O_{3-δ} ceramics for $x=0.0, 0.05$, and 0.10 (BFO100xCo) as functions of temperature. A preferred (100) crystallographic orientation and increasing average oxygen vacancies were observed in BFO5Co and BFO10Co. The Fe and Co K-edge synchrotron X-ray absorptions revealed mixed valences of Fe³⁺, Fe⁴⁺, Co²⁺, and Co³⁺ ions in BFO5Co and BFO10Co, which exhibit a ferromagnetic (or ferrimagnetic) phase below room temperature due to appearance of ferromagnetic B–O–B (B=Fe and Co) superexchange interactions. Field-cooled (FC) and zero-field-cooled (ZFC) magnetic susceptibilities exhibit a significant spin-glass splitting below room temperature in BFO5Co and BFO10Co. Two Raman-active phonon anomalies at ~ 170 K (or 200 K) and ~ 260 K were attributed to the Fe³⁺–O–Co³⁺ and Co³⁺–O–Co³⁺ magnetic orderings, respectively. This work suggests that the low-spin Co²⁺–O–Co²⁺, Fe³⁺–O–Fe³⁺ (or Fe⁴⁺), and high-spin Co²⁺–O–Co²⁺ superexchange interactions are responsible for phonon anomalies at ~ 290 (or ~ 300 K), ~ 400 , and ~ 470 K (or ~ 520 K) in BFO5Co and BFO10Co.

Keywords:

Bi(Fe_{1-x}Co_x)O₃ ceramics; Magnetic susceptibility; Phonon; Transition; Superexchange

1. Introduction

Multiferroics are promising for various sensor and memory applications because of coexistence of magnetization and ferroelectricity at room temperature and above. Bismuth ferrite BiFeO₃ is one of the most widely studied multiferroic candidates because its magnetic and ferroelectric properties appear at and above room temperature. BiFeO₃ has a G-type antiferromagnetic ordering and rhombohedral $R\bar{3}c$ space group below the Néel temperature ($T_N \sim 640$ K) and undergoes a ferroelectric-paraelectric phase transition at the Curie temperature ($T_C \sim 1100$ K) [1]. The presence of stereochemically active Bi 6s lone-pair electrons is responsible for the off-center displacement of the Bi atom from the centrosymmetric to the noncentrosymmetric structure and hence for the ferroelectricity [2]. The G-type antiferromagnetic Fe³⁺ spin spiral propagation is along the [101] direction with a rotation within the ($\bar{1}2\bar{1}$) plane [3] and its spin orientation changes in a cycloidal manner with an incommensurate periodicity of $\lambda_0 \sim 62$ nm [4,5]. The magnetoelectric coupling between the canted Fe³⁺ spins and

the polarization is essential for the cycloidal variation. Neutron diffraction of BiFeO₃ indicated a detectable modulation in Fe³⁺ cycloidal ordering below T_N [6].

Multiferroic BiCoO₃ has a tetragonal $P4mm$ symmetry below 520 K and the tetragonality ($c/a=1.27$) at room temperature is much larger than that of PbTiO₃ ($c/a=1.06$) [7]. BiCoO₃ shows an antiferromagnetic–paramagnetic transition at the Néel temperature $T_N \sim 470$ K upon heating [7]. X-ray absorption spectroscopy (XAS) showed that the high-spin Co³⁺ $3d^6$ orbital configuration prefers a G-type antiferromagnetic state in BiCoO₃ [8]. X-ray photoemission spectroscopy (XPS) and Hartree-Fock-model calculations in BiCoO₃ suggested that the combination of ferro-type orbital ordering of Co³⁺ $3d^6$ t_{2g} orbitals and the Co–O–O–Co superexchange gives rise to a C-type antiferromagnetic state [8]. In a C-type antiferromagnetic structure, the magnetic moments of the Co³⁺ ions align in the ab plane and the antiferromagnetic ab layers stack ferromagnetically along the c axis [7].

Enhanced magnetization has been reported in Bi(Fe_{1-x}Co_x)O₃ ($x=0.03$ – 0.20) with increasing Co concentration [9–14]. X-ray diffraction of Bi(Fe_{1-x}Co_x)O₃ showed that the structures are rhombohedral $R\bar{3}c$ for $x \leq 0.2$, monoclinic for $x=0.3$, and tetragonal $P4mm$ for $x \geq 0.4$ at room temperature [15]. A single-phase monoclinic Cm symmetry was reported in polycrystalline Bi(Fe_{1-x}Co_x)O₃ for $x=0.33$

Fig. 1. (a–c) SEM grain morphologies of thermally etched ceramics and (d) XRD spectra of as-sintered ceramics at room temperature. $\bar{D}$ and $\bar{A}_O$ are average grain size and oxygen atomic ratio, respectively.

and 0.37 [16]. The structural transition from the monoclinic Cm phase to the tetragonal $P4mm$ occurs gradually in a second-order manner [16]. A collinear C-type antiferromagnetic monoclinic Cm structure was reported in $\text{Bi}(\text{Fe}_{0.8}\text{Co}_{0.2})\text{O}_3$ polycrystalline ceramic [10]. A coexistence of rhombohedral and tetragonal phases was observed in $(1-x)\text{BiFeO}_3-x\text{BiCoO}_3$ thin films for $0.15 \leq x \leq 0.21$ [17,18].

The ordered double-perovskite structure, in which two different B-site cations form a superlattice, was proposed in multiferroic $\text{Bi}_2(\text{FeMn})\text{O}_6$ [19,20], $\text{Bi}_2(\text{NiMn})\text{O}_6$ [21], and $\text{Bi}_2(\text{FeCr})\text{O}_6$ [22]. Ferromagnetic (or soft ferromagnetic) and ferroelectric behaviors were reported at room temperature in $\text{Bi}_2(\text{FeCr})\text{O}_6$ [22], $\text{Bi}_2(\text{FeMn})\text{O}_6$ [23], and $\text{Bi}_2(\text{FeMo})\text{O}_6$ [24]. It was proposed that the antiferromagnetic interaction in $\text{BiMn}_{1-x}\text{Fe}_x\text{O}_3$ thin films was enhanced with suppression of ferromagnetic ordering with increasing Fe substitution [25]. A ferromagnetic ordering was observed in the multiferroic clusters in $(\text{BiFe}_{0.9}\text{Co}_{0.1}\text{O}_3)_{0.4}-(\text{Bi}_{1/2}\text{K}_{1/2}\text{TiO}_3)_{0.6}$ ceramic due to anti-parallel alignment of Fe and Co 3d electron spins [26].

Spin-phonon couplings between low-lying magnons and optical phonons have been reported in BiFeO_3 single crystals [27–33], ceramics [34,35], and thin films [36–42]. A phenomenological Landau theory suggested that the coupling between magnons and phonons (at zero wave vector) is due to zone folding [43]. Two sets of low-frequency magnon modes (ψ and ϕ) were observed in BFO to lie in and out of the cycloid plane, i.e. cyclon (ϕ) and extracyclon (ψ) modes [44]. They showed Raman anomalies in the region of 100–250 K, which were connected to a spin-reorientation transition [28,30,36,37,44]. However, neutron diffraction suggested no detectable spin magnetic anomaly in BFO crystals below room temperature and that Raman anomalies of low-lying magnons may be due to mode freezing [45,46]. Neutron scattering

suggested that dynamics of low-frequency magnons is associated with easy-axis single-ion anisotropy and the Dzyaloshinskii-Moriya interaction, which is associated with the Fe–O–Fe bond angle [47]. Thus, the correlation between phonon anomalies and magnetic-ordering transitions in BiFeO_3 still remains unclear.

This work explores the B-site Co-doping effects of magnetization and Raman-active phonon vibrations in $\text{Bi}(\text{Fe}_{1-x}\text{Co}_x)\text{O}_3$ ($x=0.0, 0.05, 0.10$) ceramics as functions of temperature. Average oxygen vacancies and oxidations of Fe and Co ions were characterized by using energy-dispersive X-ray spectroscopy (EDS) and high-resolution synchrotron X-ray absorption spectroscopy (XAS). Magnetization loops, and field-cooled (FC) and zero-field-cooled (ZFC) magnetic susceptibilities were measured to study magnetic phase and spin-glass behavior below room temperature. Back-scattering Raman spectroscopy was used to study phonon anomalies and spin-phonon couplings.

2. Experimental procedure

BiFeO_3 (BFO), $\text{Bi}(\text{Fe}_{0.95}\text{Co}_{0.05})\text{O}_{2.975}$ (BFO5Co), and $\text{Bi}(\text{Fe}_{0.90}\text{Co}_{0.10})\text{O}_{2.95}$ (BFO10Co) ceramics were prepared by the solid state reaction method, in which Bi_2O_3 , Fe_2O_3 , and CoO powders (purity $\geq 99.0\%$) were weighed in 1.1:1.0:0, 1.0:0.95:0.1, and 1.0:0.9:0.2 ratios, respectively. The CoO powder was confirmed by Raman spectroscopy, which exhibits similar vibrational modes as observed in Ref. [48]. The powders were mixed in an agate mortar with alcohol as a medium for more than 24 h. The dried mixtures were calcined at 800 °C (3 h) for all compounds and then sintered at 830 °C (10 h) for BFO, and 850 °C (3 h) for BFO5Co and BFO15Co.

Fig. 2. (a) Fe and (b) Co K-edge XANES spectra vs. photon energy and (c) Fourier transform amplitude of $k^2\chi(k)$ vs. interatomic distance for Fe K-edge XANES without phase correction. The insets are enlargements near Fe K-edge absorption peaks.

Grain morphologies and oxygen atomic ratios were measured using a Hitachi S-3400 N scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). For SEM measurement, samples were thermally etched at 800 °C for 30 min. Average grain sizes were estimated by counting the number of grains intercepted by several straight lines sufficiently long to include most of the grains on the SEM photomicrograph. Average oxygen atomic ratios were measured from 7 to 15 spots for each compound using EDS.

X-ray diffraction spectra of as-sintered ceramics were obtained using a Rigaku Multiplex Diffractometer with wavelengths $K\alpha_1$ (1.5406 Å) and $K\alpha_2$ (1.5444 Å). The Fe and Co K-edge synchrotron X-ray absorption near-edge structures (XANES) and extended X-ray absorption fine structures (EXAFS) were obtained in transmission mode at the 01C1 beam line of the National Synchrotron Radiation Research Center in Taiwan. A SQUID magnetometer (Quantum Design MPMSXL) was used to measure magnetization loops, and zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibilities ($\chi = M/H_{app}$) as functions of temperature. M and H_{app} are respectively measured magnetization and applied magnetic field. Back-scattering Raman spectra were measured using a Nanobase Model XperRam 200 Raman spectrometer equipped with a green laser of $\lambda = 532$ nm and a TE-cooled CCD detector. A Linkam THMS600 heating/cooling stage was mounted on the microscope for temperature control. The experimental cut-off frequency for our Raman spectra is around 50 cm^{-1} .

Fig. 3. Magnetization hysteresis loops at and below room temperature.

3. Results and discussion

Fig. 1(a)–(c) show grain morphologies and average grain sizes ($\bar{D}$) of 3.4, 1.45, and $2.79 \mu\text{m}$ for BFO, BFO5Co, and BFO10Co, respectively. As labeled in Fig. 1(a)–(c), the average oxygen atomic ratios ($\bar{A}_O$) for BFO, BFO5Co, and BFO10Co are respectively $52.5 \pm 1.6\%$, $49.7 \pm 0.5\%$, and $46.7 \pm 1.6\%$. The theoretical oxygen atomic ratio in the BiFeO_3 perovskite unit cell is 60%. This suggests that average oxygen vacancy concentrations increase with increasing Co substitution. As shown in Fig. 1(d), a preferred (100) crystallographic orientation was observed in the (100) and (200) peaks as Co substitution increases. This (100)-oriented crystallographic preference is consistent with the antiferromagnetic tetragonal structure in BiCoO_3 at room temperature [7]. A minor second phase of possible $\text{Bi}_2\text{Fe}_4\text{O}_9$ is present in BFO5Co as indicated by *** [49]. It was reported that BFO formed readily with a small fraction of secondary phase [50]. As illustrated by the dashed

Fig. 4. Field-cooled (FC) and zero-field-cooled (ZFC) magnetic susceptibilities in the presence of the magnetic field $H=100$ Oe.

line, XRD peaks of BFO5Co and BFO10Co shift slightly toward lower 2θ due to the larger radius (0.79 Å) of the Co^{2+} ion compared with 0.69 Å for the Fe^{3+} ion [51].

To analyze the oxidation state and interatomic correlation, the Fe and Co K-edge XANES spectra were measured as shown in Fig. 2 (a) and (b), including reference powders FeO and Fe_2O_3 . The Fe and Co K-edge XANES spectra arise primarily from the $1s \rightarrow 4p$ dipole transition [52]. As indicated by the dotted lines in the inset of Fig. 2(a), the Fe K-edge absorption peaks in BFO5Co and BFO10Co shift slightly toward higher energies than in Fe_2O_3 . The Fe K-edge absorption energy is expected to increase with increasing valence from Fe^{2+} to Fe^{4+} . This result suggests a partial valence shift of $\text{Fe}^{3+} \rightarrow \text{Fe}^{4+}$ and coexistence of Fe^{3+} and Fe^{4+} ions in BFO5Co and BFO10Co. It is consistent with the charge compensation as B-site Co^{2+} substitution increases. As shown in the inset of Fig. 2(a), a weak pre-edge peak appears in the range of 7112–7115 eV in BFO, BFO5Co, and BFO10Co due to the $1s \rightarrow 3d$ quadrupole transition. Fig. 2(b) shows the Co K-edge absorption spectra and indicates a combination of Co^{2+} and Co^{3+} valences in BFO5Co and BFO10Co as labeled by A and B [53–56]. The energy difference between A and B peaks is about 4 eV, which is close to 3 eV between CoO (Co^{2+}) and Co_2O_3 (Co^{3+}) [56]. The Co K-edge absorption peak in BFO5Co appears at slightly higher energy than in BFO10Co, confirming that BFO5Co has a higher Co^{3+} concentration. This is consistent with fewer oxygen vacancies in BFO5Co as given in

Fig. 5. Temperature-dependent Raman spectra of BFO upon heating.

Fig. 1(b) and (c). Fig. 2(c) shows the Fourier transforms of Fe K-edge EXAFS $k^2\chi(k)$ spectra and reveals interatomic distances of the Fe–O, Fe–Bi, and Fe–O–Fe bonds. The Fe–Bi and Fe–O–Fe bond lengths increase slightly as Co substitution increases and are consistent with the 2θ shifts in XRD spectra in Fig. 1(d). The magnetic orderings of Fe–O–Fe, Fe–O–Co, and Co–O–Co superexchange interactions strongly depend on 3d orbital configuration [57–59]. According to the Goodenough-Kanamori rules, the high-spin-state $\text{Fe}^{3+}(t_{2g}^3 e_g^2) - \text{O} - \text{Fe}^{3+}(t_{2g}^3 e_g^2)$, $\text{Fe}^{3+}(t_{2g}^3 e_g^2) - \text{O} - \text{Co}^{3+}(t_{2g}^4 e_g^2)$, $\text{Fe}^{3+}(t_{2g}^3 e_g^2) - \text{O} - \text{Co}^{2+}(t_{2g}^5 e_g^2)$, $\text{Co}^{2+}(t_{2g}^5 e_g^2) - \text{O} - \text{Co}^{2+}(t_{2g}^5 e_g^2)$, and $\text{Co}^{3+}(t_{2g}^4 e_g^2) - \text{O} - \text{Co}^{3+}(t_{2g}^4 e_g^2)$ 180° superexchange interactions prefer an antiferromagnetic ordering [19,59]. Ferromagnetic ordering is allowed in the $\text{Fe}^{4+}(t_{2g}^3 e_g^1) - \text{O} - \text{Fe}^{3+}(t_{2g}^3 e_g^2)$, $\text{Fe}^{4+}(t_{2g}^3 e_g^1) - \text{O} - \text{Fe}^{4+}(t_{2g}^3 e_g^1)$, $\text{Fe}^{4+}(t_{2g}^3 e_g^1) - \text{O} - \text{Co}^{2+}(t_{2g}^5 e_g^2)$, and $\text{Fe}^{4+}(t_{2g}^3 e_g^1) - \text{O} - \text{Co}^{3+}(t_{2g}^4 e_g^2)$ super-exchanges [59].

Fig. 3 shows hysteresis loops of magnetization (M) vs. magnetic field (H) at and below room temperature. A linear anti-ferromagnetic behavior was observed in BFO at 10 and 300 K. BFO5Co and BFO10Co show a ferrimagnetic-like (or soft ferromagnetic) behavior with remanent magnetizations of ~ 0.15 and ~ 0.6 emu/g at 300 K, respectively. A similar ferrimagnetic M–H loop was observed in double-perovskite $\text{Bi}_2(\text{FeMn})\text{O}_6$ thin films [23,60]. Magnetization and coercive field of BFO5Co and BFO10Co increase significantly with decreasing temperature and exhibit a typical ferromagnetic phase at 100 and 200 K. The enhancement of magnetization is likely due to appearance of ferromagnetic $\text{Fe}^{3+} - \text{O} - \text{Fe}^{4+}$, $\text{Fe}^{4+} - \text{O} - \text{Fe}^{4+}$, $\text{Fe}^{4+} - \text{O} - \text{Co}^{2+}$, and $\text{Fe}^{4+} - \text{O} - \text{Co}^{3+}$ orderings [59]. The ferromagnetic Co–O–Co double-exchange interaction may also contribute to the magnetization as Co substitution increases [61,62]. As given in Fig. 1, oxygen vacancies may play a role for increasing magnetization [63–65]. X-ray magnetic circular dichroism and density-functional-theory calculations suggested that oxygen vacancies can mediate Fe ion coupling between neighboring FeO_6 octahedral sites to induce local ferromagnetism

Fig. 6. Temperature-dependent Raman spectra of BFO5Co upon heating.

Fig. 7. Temperature-dependent Raman spectra of BFO10Co upon heating.

[63].

Fig. 4 shows zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibilities in the presence of the magnetic field $H=100$ Oe. The FC magnetic susceptibility increases with increasing Co substitution, indicating an enhancement of magnetization. This is consistent with the M-H loops as shown in Fig. 3. As shown in Fig. 4(a), BFO exhibits a slight splitting below ~ 150 K between ZFC and FC magnetic susceptibilities, suggesting a weak spin-glass characteristic [66–69]. The spin-glass behavior mainly results from magnetic frustration, deformed lattices, and random locations of magnetic ions [70]. As enlarged in the inset of Fig. 4(a), the ZFC and FC magnetic susceptibilities in BFO decreases with decreasing temperature down to ~ 150 K, and then increase as temperature decreases below ~ 150 K. As seen in Fig. 3(a), BFO remains in an antiferromagnetic phase at 10 K. The increase of magnetic susceptibility at low temperatures in Fig. 4(a) is probably caused by paramagnetic impurities. The solid line in Fig. 4(a) is a Curie-law fit below 5 K to estimate the contribution from the paramagnetic impurities, i.e. $\chi_p = C/T$ [71], with $C=4 \times 10^{-5}$ K emu/Oe g. The weak spin-glass splitting below ~ 150 K may be associated with the appearance of the paramagnetic characteristic in the antiferromagnetic matrix, which may result in local

magnetic frustration.

The splitting between ZFC and FC magnetic susceptibilities increases with increasing Co substitution as shown in Fig. 4(b) and (c) for BFO5Co and BFO10Co. Similar low-field FC and ZFC magnetization curves were reported in ferrimagnetic $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ [70] and MnCo_2O_4 [72]. The irreversible magnetization signifies a reorientation blocking of magnetic moments by spin-reversal barriers. The spin-glass phenomena can be ascribed to the frustration of competing magnetic orderings among ferromagnetic and antiferromagnetic superexchange interactions [59,61]. A significant splitting between ZFC and FC magnetizations was also observed in multiferroic $\text{Bi}(\text{Fe}_{0.5}\text{Mn}_{0.5})\text{O}_3$ thin films and $\text{BiFeO}_3/\text{BiMnO}_3$ superlattices [60]. It was classified as a spin-glass behavior due to competition between Mn-rich ferromagnetic and Fe-rich antiferromagnetic clusters [60].

For BFO5Co, the FC magnetic susceptibility exhibits a steady increase with decreasing temperature accompanied by a weak minimum at ~ 260 K as indicated by the arrow in the inset of Fig. 4 (b). This is consistent with increasing ferromagnetic (or ferrimagnetic) magnetization as temperature decreases in Fig. 3(b). The ZFC and FC magnetic susceptibilities of double-perovskite $\text{Bi}_2(\text{FeMn})\text{O}_6$ multiferroic thin film exhibited an anomaly at ~ 260 K associated

Fig. 8. Temperature-dependent Raman shifts of the $E(1)$, $E(2)$, and $A_1(1)$ modes for BFO.

with the antiferromagnetic $\text{Mn}^{3+}(t_{2g}^3 e_g^1)\text{--O--Mn}^{3+}(t_{2g}^3 e_g^1)$ ordering transition [20]. The weak susceptibility anomaly at ~ 260 K likely corresponds to the antiferromagnetic $\text{Co}^{3+}(t_{2g}^4 e_g^2)\text{--O--Co}^{3+}(t_{2g}^4 e_g^2)$ and/or $\text{Co}^{3+}(t_{2g}^5 e_g^1)\text{--O--Co}^{3+}(t_{2g}^5 e_g^1)$ orderings in the ferromagnetic matrix. The ZFC magnetic susceptibility exhibits a gradual transition from ~ 140 to ~ 200 K accompanied with a weakly temperature-dependent negative susceptibility below ~ 150 K (as indicated by the dotted line), suggesting a minor diamagnetic characteristic probably caused by the diamagnetic Bi^{3+} ions. The ZFC and FC magnetic susceptibilities in $\text{Bi}_2(\text{FeMn})\text{O}_6$ showed an anomaly at ~ 150 K due to the $\text{Fe}^{3+}\text{--O--Mn}^{3+}$ ordering [20]. As evidenced in Fig. 3(b), BFO5Co exhibit a typical ferromagnetic phase at 100 and 200 K. The transition in the region of 140–200 K is probably associated with the $\text{Fe}^{3+}\text{--O--Co}^{3+}$ ordering in the ferromagnetic matrix. The weak upturn in susceptibility below 10 K is likely due to paramagnetic impurities.

BFO10Co exhibits a similar weak minimum at ~ 270 K in the FC susceptibility as indicated by the arrow in the inset of Fig. 4(c), which likely corresponds to the antiferromagnetic $\text{Co}^{3+}\text{--O--Co}^{3+}$ ordering. As observed in BFO5Co, the ZFC magnetic susceptibility in BFO10Co exhibits a similar gradual transition in the region of ~ 130 – 220 K accompanied with a bump around 150 K in the FC susceptibility as indicated by the star in the inset of Fig. 4(c). BFO10Co exhibit a typical ferromagnetic phase at 100 and 200 K as shown in Fig. 3(c). The transition at ~ 130 – 220 K in Fig. 4(c) is probably associated with the $\text{Fe}^{3+}\text{--O--Co}^{3+}$ ordering in the ferromagnetic matrix. The $\text{Fe}^{3+}\text{--O--Co}^{3+}$ and $\text{Co}^{3+}\text{--O--Co}^{3+}$ orderings are sensitive to occupancies in the $3d$ t_{2g} and e_g orbital states of Fe

Fig. 9. Temperature-dependent Raman shifts of the $E(1)$, $E(2)$, and $A_1(1)$ modes for BFO5Co.

and Co ions [59], which are probably associated with the spin reorientation.

Figs. 5–7 show Raman vibration modes (50 – 600 cm^{-1}) as temperature increases for BFO, BFO5Co, and BFO10Co, respectively. The dashed lines illustrate frequency shifts in the major Raman-active $E(1)$, $E(2)$, $A_1(1)$ and $A_1(2)$ modes with increasing temperature. The broadness of full-width-at-half-maximum (FWHM) upon heating is mainly associated with thermal dynamic effects due to lattice anharmonicity. A Lorentzian function was used for fitting Raman profiles to acquire Raman frequency shifts and full-width-at-half-maxima (FWHMs). The rhombohedral $R3c$ primitive cell in BiFeO_3 contains two formula units. The total Γ -point phonon modes are $5A_1 + 5A_2 + 10E$, among which $4A_1 + 9E$ modes are Raman and infrared active [73–75]. The $5A_2$ modes are Raman silent and two modes ($A_1 + E$) are acoustic vibrations. Four major Raman modes appear below 250 cm^{-1} ; $E(1)$ at ~ 60 – 80 cm^{-1} , $E(2)$ at ~ 130 – 140 cm^{-1} , $A_1(1)$ at ~ 160 – 170 cm^{-1} , and $A_1(2)$ at ~ 210 – 220 cm^{-1} [73]. The vibration frequencies associated with Bi, Fe (or Co), and O atoms appear approximately below ~ 170 cm^{-1} , ~ 150 – 270 cm^{-1} , and above ~ 260 cm^{-1} , respectively [73].

Temperature-dependent Raman frequency shifts and FWHMs of the $E(1)$, $E(2)$, and $A_1(1)$ modes are plotted in Figs. 8–10 for BFO, BFO5Co, and BFO10Co, respectively. The Raman modes below 70 cm^{-1} are associated with Raman-active low-lying magnons [44]. The A_1 modes in the $R3c$ symmetry are fully symmetric with vibrations along the $[111]_c$ ferroelectric polarization direction [32,38]. The $A_1(1)$ and $A_1(2)$ modes mainly correspond to Fe (or Co) atom motions and thus are sensitive to vibrations of the Fe–O–Fe,

Fig. 10. Temperature-dependent Raman shifts of the $E(1)$, $E(2)$, and $A_1(1)$ modes for BFO10Co.

Fe–O–Co, and Co–O–Co bonds. The $E(1)$ and $E(2)$ phonon frequencies are close to the low-lying magnons and can be influenced by the spin-phonon and magnon-phonon couplings. Thus, Raman shifts of the $E(1)$, $E(2)$, $A_1(1)$, and $A_1(2)$ modes are expected to be sensitive to spin-phonon and magnetoelectric interactions.

BFO exhibits two weak Raman anomalies at ~ 160 and ~ 260 K in frequency shifts and FWHMs of the $E(1)$, $E(2)$, and $A_1(1)$ modes as indicated by the dotted lines in Fig. 8. As shown in Fig. 4(a), the FC and ZFC susceptibility revealed a minimum anomaly and weak spin-glass splitting at and below ~ 150 K respectively due to the low-temperature paramagnetic contribution in the antiferromagnetic matrix. The phonon anomaly at ~ 160 K likely corresponds to the onset of the spin-glass transition. There is no clear susceptibility anomaly around 260 K seen in Fig. 4(a). Raman anomalies of low-lying magnons (below 60 cm^{-1}) were reported in BFO crystal and thin film in the region of ~ 200 – 300 K [29,37]. The weak phonon anomaly at ~ 260 K may result from the magnon-phonon coupling.

As shown in Fig. 9, Raman shifts and FWHMs of the $E(1)$, $E(2)$,

and $A_1(1)$ modes in BFO5Co exhibit three weak and one relatively strong anomalies respectively at ~ 170 , ~ 260 , ~ 290 and ~ 470 K as indicated by the dotted lines. As shown in Fig. 4(b), the ZFC and FC magnetic susceptibilities revealed two transition anomalies at ~ 140 – 200 K and ~ 260 K due to the Fe^{3+} –O– Co^{3+} and Co^{3+} –O– Co^{3+} orderings in the ferromagnetic matrix. The weak phonon anomalies at ~ 170 and ~ 260 K can be correlated to the magnetic anomalies in Fig. 4(b). A frequency softening anomaly in the Raman mode at $\sim 143 \text{ cm}^{-1}$ was reported in CoO at the Néel temperature ($T_N \sim 290$ K), corresponding to an antiferromagnetic-paramagnetic phase transition [76,77]. The antiferromagnetic character of CoO was attributed to the Co^{2+} –O– Co^{2+} superexchange interaction between the occupied and unoccupied e_g orbital states in Co^{2+} ions [78]. The weak phonon anomaly at ~ 290 K likely correlates to the low-spin-state $\text{Co}^{2+}(t_{2g}^6 e_g^1)$ –O– $\text{Co}^{2+}(t_{2g}^6 e_g^1)$ interactions between neighboring CoO_6 octahedral sites. An antiferromagnetic-paramagnetic transition has been reported in BiCoO_3 at the Néel temperature $T_N \sim 470$ K [7]. The phonon anomaly at ~ 470 K probably correlates to the antiferromagnetic high-spin-state Co^{2+} –O– Co^{2+} ordering [19–22].

For BFO10Co, Raman shifts and FWHMs of the $E(1)$, $E(2)$, and $A_1(1)$ modes exhibit five anomalies at ~ 200 , ~ 260 , ~ 300 , ~ 400 , and ~ 520 K as indicated by the dotted lines. As evidenced in Fig. 4(c), the ZFC and FC magnetic susceptibilities suggest two transitions at ~ 130 – 220 K and ~ 270 K caused by the Fe^{3+} –O– Co^{3+} and Co^{3+} –O– Co^{3+} orderings, respectively. The weak phonon anomalies at ~ 200 and ~ 260 K are likely due to the transitions of Fe^{3+} –O– Co^{3+} and Co^{3+} –O– Co^{3+} orderings, respectively. As discussed in BFO5Co, the phonon anomaly at ~ 300 K likely correlates to a transition of the low-spin-state Co^{2+} –O– Co^{2+} magnetic orderings. Magnetization of double-perovskite $\text{Bi}_2(\text{FeMn})\text{O}_6$ multiferroic thin films exhibited a sequential anomaly at ~ 440 K, which was attributed to a transition of antiferromagnetic Fe^{3+} –O– Fe^{3+} ordering [20]. A partial $\text{Fe}^{3+} \rightarrow \text{Fe}^{4+}$ valence shift was revealed in BFO5Co and BFO10Co as shown in Fig. 2. Because only one unpaired electron occupies the e_g orbital state in the $\text{Fe}^{4+} 3d^4(t_{2g}^3 e_g^1)$ configuration, the $\text{Fe}^{3+}(t_{2g}^3 e_g^2)$ –O– $\text{Fe}^{4+}(t_{2g}^3 e_g^1)$ and $\text{Fe}^{4+}(t_{2g}^3 e_g^1)$ –O– $\text{Fe}^{4+}(t_{2g}^3 e_g^1)$ superexchange interactions are weaker than the $\text{Fe}^{3+}(t_{2g}^3 e_g^2)$ –O– $\text{Fe}^{3+}(t_{2g}^3 e_g^2)$ and thus may correspond to a lower ordering transition temperature. Thus, the phonon anomaly at ~ 400 K in BFO10Co likely corresponds to the onset of the Fe–O–Fe (Fe^{3+} or Fe^{4+}) ordering transition. Concerning the phonon anomaly at ~ 520 K, as discussed for the phonon anomaly at ~ 470 K in BFO5Co, it is likely associated with the high-spin $\text{Co}^{2+}(t_{2g}^5 e_g^2)$ –O– $\text{Co}^{2+}(t_{2g}^5 e_g^2)$ interaction which is stronger than the high-spin-state $\text{Fe}^{3+}(t_{2g}^3 e_g^2)$ –O– $\text{Fe}^{3+}(t_{2g}^3 e_g^2)$. The high-spin Co^{2+} –O– Co^{2+} ordering can be enhanced as Co substitution increases. Hence, the transition caused by the high-spin-state Co^{2+} –O– Co^{2+} ordering shifts toward higher temperature (~ 520 K) in BFO10Co. To compare the correlation between various magnetic orderings and phonon anomalies, a summary is given in Table 1 for BFO5Co and BFO10Co in terms of phonon transition temperatures and proposed B–O–B ($\text{B} = \text{Fe}$ and Co) magnetic orderings.

Table 1. Summary of phonon transition temperature and proposed B–O–B ($\text{B} = \text{Fe}$, Co) magnetic orderings in ferromagnetic matrix for BFO5Co and BFO10Co. “w” and “s” (in brackets) indicate relatively weak and strong phonon anomalies.

B–O–B ordering	Fe^{3+} –O– Co^{3+}	Co^{3+} –O– Co^{3+}	low-spin Co^{2+} –O– Co^{2+}	Fe–O–Fe (Fe^{3+} or Fe^{4+})	high-spin Co^{2+} –O– Co^{2+}
BFO5Co	~ 170 K (w)	~ 260 K (w)	~ 290 K (w)		~ 470 K (s)
BFO10Co	~ 200 K (w)	~ 260 K (w)	~ 300 K (w)	~ 400 K (s)	~ 520 K (w)

4. Conclusions

BFO remains in an antiferromagnetic phase with a minor paramagnetic characteristic in the low-temperature region. A typical ferromagnetic phase was revealed in BFO5Co and BFO10Co below room temperature. The Fe and Co K-edge synchrotron X-ray absorptions revealed mixed valences of Fe^{3+} , Fe^{4+} , Co^{2+} , and Co^{3+} ions in BFO5Co and BFO10Co. The enhanced magnetization in BFO5Co and BFO10Co was attributed to ferromagnetic $\text{Fe}^{4+}\text{--O--Fe}^{4+}$, $\text{Fe}^{4+}\text{--O--Fe}^{3+}$, $\text{Fe}^{4+}\text{--O--Co}^{3+}$, and $\text{Fe}^{4+}\text{--O--Co}^{2+}$ superexchange couplings. The FC and ZFC magnetic susceptibilities reveal a spin-glass splitting behavior below room temperature, which was enhanced as Co substitution increases. The gradual susceptibility transitions at $\sim 130\text{--}220\text{ K}$ in BFO5Co and BFO10Co are probably associated with the $\text{Fe}^{3+}\text{--O--Co}^{3+}$ ordering in the ferromagnetic matrix. Two phonon anomalies at $\sim 160\text{--}200\text{ K}$ and $\sim 260\text{ K}$ were attributed to magnetic orderings caused by $\text{Fe}^{3+}\text{--O--Co}^{3+}$ and $\text{Co}^{3+}\text{--O--Co}^{3+}$ interactions, respectively. Additional phonon anomalies were observed in BFO5Co and BFO10Co at ~ 290 , ~ 400 , and $\sim 470\text{ K}$ (or $\sim 520\text{ K}$) and were attributed to the low-spin $\text{Co}^{2+}(t_{2g}^6 e_g^1)\text{--O--Co}^{2+}(t_{2g}^6 e_g^1)$, Fe^{3+} (or $\text{Fe}^{4+})\text{--O--Fe}^{3+}$ (or $\text{Fe}^{4+})$, and high-spin $\text{Co}^{2+}(t_{2g}^5 e_g^2)\text{--O--Co}^{2+}(t_{2g}^5 e_g^2)$ superexchange interactions, respectively.

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