Experimental and theoretical studies on induced ferromagnetism of new \((1 - x)\) \(\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3 + x\text{BaFeO}_3 - \delta\) solid solution

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New solid solution of \(\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\) with \(\text{BaFeO}_3 - \delta\) materials were fabricated by sol–gel method. Analysis of X-ray diffraction patterns indicated that \(\text{BaFeO}_3 - \delta\) materials existed as a well solid solution and resulted in distortion the structure of host \(\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\) materials. The randomly incorporated Fe and Ba cations in the host \(\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\) crystal decreased the optical band gap from 3.11 to 2.48 eV, and induced the room-temperature ferromagnetism. Our density-functional theory calculations further suggested that both Ba for Bi/Na-site and Fe dopant, regardless of the substitutional sites, in \(\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\) lead to the induced magnetism, which is illustrated in terms of the exchange splitting between spin subbands through the crystal field theory and Jahn–Teller distortion effects. Our work proposes a simple method for fabricating lead-free ferroelectric materials with ferromagnetism property for multifunctional applications in smart electronic devices.

The current research trend in materials science is injecting ferromagnetism into ferroelectric materials to create next-generation smart electronic devices\(^{12}\). The development of ferromagnetism materials based on lead-based ferroelectric by doing transition metals, such as \(\text{PbTiO}_3\), has been hampered because their materials strong adverse effect on the environment and human health\(^3\). Ferroelectric lead-based \(\text{PbTiO}_3\) materials are more commonly used than lead-free ferroelectric materials, such as those based on \(\text{Bi}_2\text{(Na,K)}_2\text{TiO}_5\), \(\text{K,Na})\text{NbO}_3\), or \((\text{Ba,Ca})(\text{Zr,Ti})\text{O}_3\)\(^{4,5}\). \(\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\) as one of common lead-free ferroelectric compounds has been considered as a promising candidate that can be replacement for lead-based substances because of its stronger polarization\(^3\). Therefore, injecting room-temperature ferromagnetism into lead-free ferroelectric \(\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\) is one of significant research interests.

Scholars have developed \(\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\)-based materials with room-temperature ferromagnetism property by using transition metals, such as \(\text{Co}, \text{Fe}, \text{Mn}, \text{or Cr}\)\(^{8-11}\). Moreover, the solid solutions of \(\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\)-based materials with \(\text{BiFeO}_3\) material exhibits room-temperature ferromagnetism\(^{12}\). \(\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\) materials are composed of ferrite compounds, such as \(\text{CoMn}_2\text{Fe}_3\text{O}_4\)\(^{13}\). Ju et al. predicted that substituting a transition metal cation to Ti-site results in the magnetic moments because of the spin polarization of the 3d electrons in the transition metal\(^{14}\). However, the origin of ferromagnetism in transition metal doped lead-free ferroelectric materials were still debated. The pure \(\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\) materials exhibited the weak-ferromagnetism at room temperature which were possible explained by the surface-effect and/or self-defect\(^{15,16}\). Zhang et al. predicted that Na and Ti vacancies induced the magnetization rather than Bi or O vacancies\(^{15}\). Ju et al. reported that Na vacancies located at/near the surface of nanograins of nanocrystalline \(\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\) materials possibly displayed the ferromagnetism\(^{16}\). Such predictions were well consisted with recent obtained room temperature ferromagnetism in pure \(\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\) materials\(^{10,11}\). However, the magnetization of pure \(\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\) materials are quite small,

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normally less than 1 menu/g, which hinted to apply in electronics devices. Injection of transition metal into host lead-free ferroelectric Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials possibly enhanced the magnetization up to ~9 menu/g. Unlike the picture of ferromagnetism at room temperature of pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$, a various magnetism sources were injected to lead-free ferroelectric materials which resulted in the room temperature ferromagnetism; such as the O-vacancies (in case of Cr-doped Na$_{0.5}$Bi$_{0.5}$TiO$_3$), magnetic clusters (in case of Co-doped Na$_{0.5}$Bi$_{0.5}$TiO$_3$), or interaction of magnetic cations through oxygen vacancies as intrinsic phenomenon (in case of Fe-, Mn-doped Na$_{0.5}$Bi$_{0.5}$TiO$_3$). Therefore, the origin of room temperature ferromagnetism needs to be deep understood to control the magnetization for smart-electronic devices application.

Thank to well solid solution of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ material with various type of ABO$_3$ dopant materials, the physical properties of host Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials were enhanced$^{17-27}$. Rahman et al. reported that both ferroelectric and piezoelectric properties of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ increased via solid solution of BaZrO$_3$ where the both remanent polarization and piezoelectric constant increased from 22 μC/cm$^2$ and 60 pC/N for pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ to 30 μC/cm$^2$ and 112 pC/N for 4 mol% BaZrO$_3$ solid solution in Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials$^{17}$. Yang et al. reported that the (Ba$_{x}$Fe$_{1-x}$)$_3$TiO$_9$ solid solution in host Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials resulted in greatly lowered coercive field without degrading remanent magnetization$^{28}$. Bai et al. reported that the Bi(Fe$_{0.75}$Ti$_{0.25}$O$_{3.08}$ (Me = Zn, Ni, Mg, Co)-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials displayed the large strain response (>0.3%) with a high normalized strain (s$_{max}$/σ$_{max}$ > 550 pm/V)$^{29}$. Zhou et al. reported that BaNbO$_3$ diffused into lattice of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ to form a solid solution resulted in enhancement of the dielectric properties of host Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials$^{30}$. Kaswan et al. reported on ferromagnetism in Bi$_{1.4}$Na$_{0.6}$TiO$_3$-Ba$_6$Bi$_3$Fe$_{12}$O$_{39}$ composites materials$^{31}$. Pattanayak et al. observed the ferromagnetic properties of a BaFe$_2$O$_4$-modified Bi$_0.5$Na$_{0.5}$TiO$_3$ system$^{32}$. Recently, Singh et al. reported on the ferromagnetic properties of Bi$_0.3$Na$_{0.7}$TiO$_3$ materials induced by the addition of LaFeO$_3$ as solid solution$^{33}$. In addition, the magnetic properties of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials were found to be strong enhancement such magnetization via solid solution with various impurities materials (e.g. Mn$_{0.04}$Ti$_{0.96}$O$_2$, Fe$_{0.04}$Ti$_{0.96}$O$_2$, Co$_{0.04}$Ti$_{0.96}$O$_2$, or Ti$_{0.96}$O$_2$) or perovskite-type materials (e.g. MgFe$_{0.2}$O$_{0.8}$, SrFe$_{0.2}$O$_{0.8}$, CaMn$_{0.8}$O$_{0.2}$, or Mn$_{0.2}$Ti$_{0.8}$) materials$^{34-38}$. The double perovskite-type structural materials contained the transition metals (e.g. Bi(Fe$_{1-x}$Zn$_x$)$_{3}$O$_{9.1}$, Bi(Fe$_{1-x}$Mn$_x$)$_{3}$O$_{9.1}$, Bi(Fe$_{1-x}$Co$_x$)$_{3}$O$_{9.1}$, or Bi(Fe$_{1-x}$Ni$_x$)$_{3}$O$_{9.1}$) were also reported to enhance the magnetic properties of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials when their materials were solid solution into host materials$^{39-42}$. The magnetization of modified- Na$_{0.5}$Bi$_{0.5}$TiO$_3$ samples via impurities of ilmenite-type materials, perovskite-type or double perovskite structural materials were found to have large magnetization moment which were compared with single transition metal dopants$^{39-42}$.

Among alkaline-earth iron perovskite A$_{2}$FeO$_{3-\delta}$ family (Ae = Ba, Ca, Sr, and Mg), BaFeO$_{3-\delta}$ is one of interesting materials because its ferromagnetic domains could be controllable by an applied magnetic field$^{43}$. BaFeO$_{3-\delta}$ materials exhibited complex of phase such as monoclinic, rhombohedral, pseudo-cubic and cubic which depended on the valence state of Fe and transition between them$^{43}$. Mori et al. reported that BaFeO$_{3-\delta}$ compounds existed in many forms such hexagonal phase in a wide range of oxygen content BaFeO$_{2.63-2.92}$ while other phases have existed such triclinic I, Fe$_{2}$O$_{3}$, triclinic II, Fe$_{2}$O$_{5}$(64-67), rhombohedral I and II, Fe$_{2}$O$_{5}$(62-64)$^{45}$ and tetragonal, BaFe$_{2}$(75-2.41)$^{45}$. The cubic perovskite BaFeO$_3$ with Fe$^{3+}$ state has A-type spin structure as ferromagnetism below 111 K$^{46}$. Clemens et al. reported that BaFeO$_{3.5}$ materials with Fe$^{3+}$ state exhibited the G-type antiferromagnetic structure with Neel temperature of 720 K$^{45}$. Delattre et al. reported that the BaFe$_{2}$O$_{4}$ with orthorhombic structural exhibited the strong couple antiferromagnet$^{48}$. Theoretical simulation predicted that the BaFeO$_3$ materials has tetragonal symmetry and the G-type antiferromagnetic spin configuration$^{49}$. The highest ferromagnetic ordering was found around 235 K in BaFeO$_{3-\delta}$ were obtained for thin film growing on the SrTiO$_3$ substrate$^{45}$. Recently, the new system of (1-x)Na$_{0.5}$Bi$_{0.5}$TiO$_3$ + xFeO$_{3-\delta}$ (Ae = Sr, Ca, and Mg) materials as solid solution was successful fabricated by using the sol–gel technique$^{36,38}$. The results provided that the impurity cation (such as Sr, Mg) and Fe random incorporated with (Bi,Na)-site and Ti-site, respectively, were exhibited the strong ferromagnetism at room temperature where the magnetization were found to great enhancement than that of single transition metal dopants which were possible resulted from co-modification at A-site via alkaline-earth and Fe cation at B-site of host Na$_{0.5}$Bi$_{0.5}$TiO$_3$$^{28,30}$. In the periodic table of elements, Ba is the largest radius in alkaline earth metals, thus, we expected that the co-modification of Ba cations at A-site and Fe cations at B-site, respectively, of host Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials resulted exhibition large magnetization during solid solution of BaFeO$_{3-\delta}$ into Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials.

In this work, new system (1-x)Na$_{0.5}$Bi$_{0.5}$TiO$_3$ + xBaFeO$_{3-\delta}$ materials as solid solution were fabricated by sol–gel method. The BaFeO$_{3-\delta}$ materials were well solid solution into the host Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials through diffusion and random incorporation of Ba and Fe cations with host lattice of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials. The structural distortion and reduced optical band gap of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials were obtained. The complex magnetic properties of BaFeO$_{3-\delta}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials was obtained as function of BaFeO$_{3-\delta}$ amounts addition.

**Results and discussion**

Figure 1a, b shows the EDS spectral of pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ samples and BaFeO$_{3-\delta}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ samples with 5 mol.% BaFeO$_{3-\delta}$, respectively. The inset of each figure showed the selected area for EDS elements characterization. All expectational elements such Bi, Na, Ti and O were obtained in EDS spectral of pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ samples, as shown in Fig. 1a. The addition of the Ba and Fe peaks were showed in the EDS spectral of BaFeO$_{3-\delta}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ samples, as expected, which were presented at the Fig. 1b. The results provided that the BaFeO$_{3-\delta}$ impurities existed in our samples.

The chemical maps of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials modified with 9 mol.% BaFeO$_{3-\delta}$ were analyzed. The distribution of impurity elements in the Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials modified with 9 mol.% BaFeO$_{3-\delta}$ is shown in Fig. 2. The surface morphology of the area selected for chemical mapping is shown in Fig. 2a, whereas Fig. 2b presents the total contribution of all of the chemical elements in the sample. The partial chemical maps of Bi, Na, Ti, O,
Ba, and Fe elements are shown in Fig. 2c–h, respectively. The results clearly demonstrated that the constituent chemical elements were homogenously dispersed in the sample.

Figure 3 (a) shows the X-ray diffraction patterns of pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ and BaFeO$_{3-\delta}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials with various BaFeO$_{3-\delta}$ concentrations. On the basis of diffraction peak position and relative to intensity, all samples were indexed to a perovskite structure with the rhombohedral symmetry of the Na$_{0.5}$Bi$_{0.5}$TiO$_3$ compound (JCPDS card no. 00–036-0340, space group R3c). In addition, the impurities phase or phase segregation was not founded in the X-ray diffraction patterns. All X-ray diffraction pattern of BaFeO$_{3-\delta}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ samples were indexed to follow the structural of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ compound. The results indicated that BaFeO$_{3-\delta}$ materials exhibited a well solid solution in Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials. In other word, the Ba and Fe cations were diffused to randomly incorporate with host lattice of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ compound as solid solution. In order to

Figure 1. The EDS spectral of (a) pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials, and (b) BaFeO$_{3-\delta}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials with 5 mol% BaFeO$_{3-\delta}$ as solid solution. The inset of each figure shown the selected area for composition characterization.

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character the influence of Ba and Fe into host crystalline of Na0.5Bi0.5TiO3 compound, the diffraction angle of pure Na0.5Bi0.5TiO3 and BaFeO3−δ-modified Bi0.5Na0.5TiO3 samples was magnified within 31.0° to 34.0° for setline (012)/(110) peaks, as shown in Fig. 3b. The setline peaks were overloaded together which were distinguished via Lorentz fitting, as shown in dot line of Fig. 3b. The results clearly indicated that the diffraction peaks of Na0.5Bi0.5TiO3 materials trended to shift to lower diffraction angle as increasing the BaFeO3−δ amounts, which provided the evident for expansion of lattice parameter. Furthermore, the lattice parameters a and c of the pure Bi0.5Na0.5TiO3 and the BaFeO3−δ-modified Bi0.5Na0.5TiO3 as a function of BaFeO3−δ addition amounts are shown in Fig. 3c. The results show that the distorted lattice parameters of the Bi0.5Na0.5TiO3 compound are not a linear function of the concentrations of the BaFeO3−δ solid solution, which showed complex lattice parameter distortion. This result could be attributed to the different radii of Ba and Fe cations in the additives and that of Bi, Na, and Ti incorporated randomly in the lattice of the host Na0.5Bi0.5TiO3 materials. Based on the Shamon’ reported, the radius of Ba2+ and Fe2+/3+ cations were 1.61 Å and 0.645 Å/0.780 Å, respectively, while the radius of Bi3+, Na+ and Ti4+ cations were 1.17 Å, 1.39 Å and 0.605 Å, respectively51. Therefore, the Fe cations diffused to substitute for Ti-sites in perovskite structural of Na0.5Bi0.5TiO3 crystal, resulted in expansion of the lattice. The fact that the radius of Ba2+ cations are larger than that of both Bi3+ and Na+ cations were also reflected by expanding the lattice parameter of host Na0.5Bi0.5TiO3 compound. However, we noted that the oxygen vacancies were generated due to unbalance of valence states of Fe2+/3+ and Ti4+ at B-site and Ba2+ for Bi3+ at A-site. In addition, the Na vacancies were created when Ba2+ substitute Na+. The oxygen vacancies (v) has radius of 1.31 Å which were smaller than that of oxygen anion (O2−) of 1.4 Å52. Therefore, the existence of oxygen vacancies in the structure led to reduction of the lattice parameter. The structural distortion of Na0.5Bi0.5TiO3 materials was due to co-modification at A- and B-site via alkali earth and transition metal, respectively, which was consistent with recently reported28–30. In other word, the X-ray diffraction characterization of BaFeO3−δ-modified Na0.5Bi0.5TiO3 samples provided that the BaFeO3−δ materials were well solid solution into host Na0.5Bi0.5TiO3 materials.

Figure 4a show the Raman scattering of pure Na0.5Bi0.5TiO3 materials and BaFeO3−δ-modified Na0.5Bi0.5TiO3 materials with various of BaFeO3−δ concentration as solid solutions at room temperature. The results provide that the shape of Raman scattering spectra seem to be unchanged in comparison between that of pure Na0.5Bi0.5TiO3 materials and that of BaFeO3−δ-modified Na0.5Bi0.5TiO3 materials. In the wave number ranging from 300 cm−1 to 1000 cm−1, the Raman spectra were possible divided into three main regions and they overlapped each other. The three main band regions were in the range of 300–450 cm−1, 450–700 cm−1 and 700–1000 cm−1, respectively. The combination of experimental investigation and first principles density functional theoretical calculation for Raman vibration modes of Na0.5Bi0.5TiO3 materials exhibited that the lowest frequency modes in range of

![Figure 3.](https://www.nature.com/scientificreports/)

(a) X-ray diffraction pattern of BaFeO3−δ solid solution into Na0.5Bi0.5TiO3 with various concentrations within the 2θ range of 20° to 70°; (b) magnified X-ray diffraction within 2θ range of 31°–34° for comparing setline (012)/(110) peaks; and (c) dependence of the lattice parameters of pure Bi0.5Na0.5TiO3 and BaFeO3−δ-modified Bi0.5Na0.5TiO3 samples on the amounts of BaFeO3−δ solid solution.
246–401 cm⁻¹ are dominated by TiO₆ vibrations, and the higher frequency modes in the range 413–826 cm⁻¹ are primarily associated with the oxygen atoms vibrations. The random occupation at A-sites of Bi and Na resulted in overlap of Raman scattering peaks in range of 109–134 cm⁻¹ and 155–187 cm⁻¹, which were originated from Bi-O and Na–O vibration modes, respectively. In addition, Chen et al. reported that the vibration of Ti–O bonds is related to the wave number in range of 200–400 cm⁻¹ while the vibration of TiO₆ octahedra is assigned to the wave number regions from 450 cm⁻¹ to 700 cm⁻¹. The overlapping of Raman scattering modes was hard to characterize the influence of Ba and Fe into vibration modes of host lattice Na₀.₅Bi₀.₅TiO₃ materials. Therefore, we tried to distinguish the Raman scattering modes via the fitting with Lorentz functions (with correction of fitting over 0.99). The deconvolution Raman scattering modes (blue line) of pure Na₀.₅Bi₀.₅TiO₃ samples and BaFeO₃−δ-modified Na₀.₅Bi₀.₅TiO₃ samples as shown in Fig. 4b. The eight Raman scattering vibrational modes were obtained for both pure Na₀.₅Bi₀.₅TiO₃ and BaFeO₃−δ-modified Na₀.₅Bi₀.₅TiO₃ samples. The results were well consistent with recently observation in vibration of Raman scattering modes of perovskite-type structural AeFeO₃−δ family-modified Na₀.₅Bi₀.₅TiO₃ materials. The vibration modes at around 595 cm⁻¹ (red dot line marked in the Fig. 4b) trended to shift to high frequency, which were suggested to be related to distorted structure of (Ti,Fe)O₆ framework and/or effective mass effect because of difference between the radius and mass of impurities Fe and host Ti at B-site. In other word, the shifted Raman scattering modes confirmed the substitution of Ba and Fe into the host lattice Na₀.₅Bi₀.₅TiO₃ materials.

Figure 5a shows the optical absorption spectra of pure Na₀.₅Bi₀.₅TiO₃ and BaFeO₃−δ-modified Na₀.₅Bi₀.₅TiO₃ with various BaFeO₃−δ concentrations. Pure Na₀.₅Bi₀.₅TiO₃ samples exhibited a single absorbance edge, consistent with the reported optical properties of Na₀.₅Bi₀.₅TiO₃ materials. However, pure Na₀.₅Bi₀.₅TiO₃ materials exhibited the unsharp transition which were tailored with slightly tail. The small tail at long wavelength in absorbance spectroscopy of pure Na₀.₅Bi₀.₅TiO₃ materials were suggested to be related with self-defect and/or surface effect cause of unsaturation bonding pair of atoms at the surface. The addition BaFeO₃−δ to Na₀.₅Bi₀.₅TiO₃ material as solid solution led to a red shift of the absorbance edge. The appearance of peaks around 485 nm in...
Na$_{0.5}$Bi$_{0.5}$TiO$_3$-based material was possibly a result of changes in the bonding type between hybridizations in the middle electronic band structure of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials$^{28-30,57}$. Optical band gap ($E_g$) values of pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ and BaFeO$_{3-δ}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials were calculated using the plot of $(a$hν$)^2$ versus photon energy $hν$, as shown in Fig. 5b, where $a$, $h$ and $ν$ are the absorbance coefficient, the Planck constant and the frequency, respectively. The band gap energy of pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials were estimated to be approximately 3.09 eV, whereas that of BaFeO$_{3-δ}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials exhibited value of 2.48 eV for 9 mol.% BaFeO$_{3-δ}$ solid solution in host Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials. The detail dependence of $E_g$ values of BaFeO$_{3-δ}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ compound as function of BaFeO$_{3-δ}$ concentration is shown in the inset of Fig. 5b. The optical band gap of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ material in which the Ti-sites substituted with the transition metal, as $B$-site modified, decreased in lead-free ferroelectric Bi-based materials; this phenomenon could be due to the presence of new local states in the electronic structure of both the highest occupied molecular orbital and the lowest unoccupied molecular orbital in the total band structure$^{9-11,14,57}$. In addition, the reduced optical band gap in $A$-site modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$-based material was possibly a result of changes in the bonding type between hybridizations $A$-$O^{58}$. Oxygen vacancies created because of unbalanced charges between impurities and hosts (e.g. Fe$^{2+}$/3+) substitue for Ti$^{4+}$, and Ba$^2+$ replacement for Bi$^{3+}$ also led to the reduction in the optical band gap because the oxygen vacancy states normally located below and near the conduction band$^{9-11,59,60}$. Thus, we suggest that the random substitution of Ba and Fe ions into the host Na$_{0.5}$Bi$_{0.5}$TiO$_3$ could alter the electronic band structure, resulting in reduction of the optical band gap.

Figure 6a shows the room-temperature PL emission spectra of pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ and BaFeO$_{3-δ}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ samples with various BaFeO$_{3-δ}$ amount. The PL spectral of all samples exhibited a broad band emission while strong emission showed in range from 479 to 505 nm. The addition of BaFeO$_{3-δ}$ into host Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials as solid solution suppressed the emission peak, as shown in inset of Fig. 6a. However, we noted that a slight addition of BaFeO$_{3-δ}$ concentration enhanced the emission intensity. In addition, the PL spectral of pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ and BaFeO$_{3-δ}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ samples was overlapped together, suggesting to multi-emission peaks with closed together. Thus, we tried to distinguish the multi-emission peaks via Lorentz fitting. The deconvoluted emission peaks of pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ samples were shown in Fig. 6b. The broad band visible luminescence was also recently reported for ferroelectric titanates-based materials at room temperature such as BaTiO$_3$, SrTiO$_3$, PbTiO$_3$, etc.$^{61}$ The observations in broad band emission were also archived in Bi$_5$K$_2$Ti$_7$O$_{24}$ materials, which were related to the surface effect and/or self-defect effect$^{62}$. Normally, the coordination status of the atoms at the surface of materials is unsaturated, resulting in unpaired states, that make them different from that in the bulk$^{48}$. The unsaturated atoms that existed at the surface region of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials formed local levels in the forbidden gaps, this displayed the effect of the self-trapped excitons$^{63}$. Therefore, the incident photon was absorbed by the Na$_{0.5}$Bi$_{0.5}$TiO$_3$ powder as it is illuminated with the excited source. The absorption photons could create some localized levels and form small polarons. The interaction between the holes in the valence band and polarons formed by the intermediate self-trapped excitons caused blue shift of the luminescence$^{64}$. In addition, the structural distortion because of coupling of TiO$_6$-$\rightarrow$TiO$_6$ adjacent octahedra generate the localized electronic levels above the valence band. The recombination from these levels may result in the photoluminescence of Bi$_5$K$_2$Ti$_7$O$_{24}$ materials$^{45}$. The photoluminescence of ferroelectric materials is not generally governed by band-to-band transition, owning to the difficulty in recombination of electron–hole pairs and the separation of the natural polarization domain in the materials. In this kind of materials, the surface states were in charge of the luminescence, in which many unsaturated atoms that presented on the surface of the ferroelectric materials creates the localized levels in the forbidden gaps. Interestingly, the intensity of PL emission of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials was suppressed by the addition of BaFeO$_{3-δ}$, as shown in the inset of Fig. 6b. The PL emission spectra of BaFeO$_{3-δ}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials did not change, indicating the lack of Ba and Fe substitution at the $A$- and $B$-sites, respectively, in the new electron–hole transitions. Thus, the substitution of Fe cation with Ti at the octahedral sites created oxygen vacancies; such vacancies acted as the chapping electron.

![Figure 6](https://doi.org/10.1038/s41598-021-88377-3)
Figure 7. $M-H$ curves at room temperature of (a) undoped Na$_{0.5}$Bi$_{0.5}$TiO$_3$, and BaFeO$_{3-\delta}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ samples with (b) 0.5 mol%, (c) 1 mol%, (d) 3 mol%, (e) 5 mol%, (f) 7 mol% and (g) 9 mol% BaFeO$_{3-\delta}$ as solid solution. Inset of (a) shown the M-H curve of pure Bi$_{0.5}$Na$_{0.5}$TiO$_3$ material after substrate diamagnetic components.

generated from absorbance photon energy, thereby prevented the recombination of the electron–hole pairs to generate photons.

Furthermore, the role of BaFeO$_{3-\delta}$ solid solution in Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials in imparting magnetism was dependent on the applied magnetic field at room temperature, as shown in Fig. 7a–g for pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ and BaFeO$_{3-\delta}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials with BaFeO$_{3-\delta}$ concentration of 0.5, 1, 3, 5, 7 and 9 mol%, respectively. The pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ exhibited the anti-$S$-shape in $M-H$ curves, indicating the combination of diamagnetism and weak ferromagnetism, as shown in Fig. 7a. The diamagnetism in pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ samples originated from the electronic configuration of Ti$^{4+}$ as $3d^0$, whereas the weak ferromagnetism originated from self-defects$^{9,11,14,16,30,64,65}$. The typical hysteresis loop of ferromagnetism was obtained for pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials after subtract the diamagnetic components, as shown in inset of Fig. 7a. The saturation magnetization was estimated around 1.5 memu/g which were well consisted with recently reported by Ju et al.$^{16}$. In addition, the remanent magnetization ($M_r$) and coercive field ($H_C$) of pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials were approximately 0.11 memu/g and 73 Oe, respectively, which were solid evidence for presentation of ferromagnetic state at room temperature. The estimation for their values were also performed with recently reported by Thanh et al. and Ju et al. which those were possibly originated from self-defect such as Na-, Ti- or O-vacancies$^{10,16}$. The $M-H$ curves trend to switch from anti-$S$-shape to $S$-shape in the BaFeO$_{3-\delta}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ samples as the BaFeO$_{3-\delta}$ concentration in the solid solution increase, providing evidence regarding the strength enhancement of ferromagnetic ordering in the samples. As shown in Fig. 7c, the typical ferromagnetic hysteresis loops were obtained where the magnetization trended to saturate as the external applied magnetic field increase, and the strength of ferromagnetic increase. However, further increasing amounts of BaFeO$_{3-\delta}$ into host Na$_{0.5}$Bi$_{0.5}$TiO$_3$, the $M-H$ curves exhibited the unsaturation with low applied external magnetic field, as shown in Fig. 7d–g. The dependence of shape in magnetic hysteresis loop of BaFeO$_{3-\delta}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials represented that the magnetic properties of BaFeO$_{3-\delta}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials were very complex, on the one hand the magnetic properties of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials were strong dependent of the concentration of BaFeO$_{3-\delta}$ as solid solution. The $M_r$ and $H_C$ values of BaFeO$_{3-\delta}$-modified Bi$_{0.5}$Na$_{0.5}$TiO$_3$ materials were approximately 51–106 Oe and 0.12–0.48 memu/g, respectively. These results were consistent with the recently observed $M_r$ and $H_C$ of transition-metal-doped lead-free and lead-based ferroelectric materials$^{8,11,60,64-68}$. The nonzero $M_r$ and $H_C$ values of BaFeO$_{3-\delta}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials provided solid evidence for the presence of the ferromagnetic state at room temperature. In addition, the maximum magnetization was estimated around 23 memu/g for 9 mol% BaFeO$_{3-\delta}$ solid solution in host Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials. That value was larger than that of self-defect induced magnetism of pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials or single transition metals doped Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials, in which around ~ 1.5 memu/g for Cr-doped Na$_{0.5}$Bi$_{0.5}$TiO$_3$, ~ 3 memu/g for Co-doped Na$_{0.5}$Bi$_{0.5}$TiO$_3$, ~ 9 memu/g for Mn-doped Na$_{0.5}$Bi$_{0.5}$TiO$_3$, ~ 15 memu/g for Fe-doped Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials, and ~ 4 memu/g for Ni-doped Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials$^{8,11,60,68}$. Herein, we need to remark that the origin of ferromagnetic ordering of transition metal impurities containing Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials at room temperature were still debated. The weak-ferromagnetism in pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials were possibly originated from self-defect and/or surface defect (such as Ti and Na-vacancies) while the magnetization of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials were slightly enhanced via oxygen vacancies$^{11,14,16,30}$. The Mn-, Ni- and Fe-doped Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials exhibited the room temperature ferromagnetism which were related to intrinsic phenomenon where the transition cations such of Mn, Ni and Fe interacted with the oxygen vacancies, like F-center interaction mechanism, e.g. Mn$^{2+}$...–n–Mn$^{2+}$ or Fe$^{2+}$...–n–Fe$^{2+}$ pairs etc., which were favored for ferromagnetic ordering$^{8,11,60,64}$. Unlike Mn-, Ni- and
Fe-cations impurities in Na_{0.5}Bi_{0.5}TiO_{3} materials, the Co impurities tend to form Co-clusters embedding in host Na_{0.5}Bi_{0.5}TiO_{3} materials which displayed the room temperature ferromagnetism. Recently, our experimental observation along with first principle calculation predicted that the interaction of Co cations into host Na_{0.5}Bi_{0.5}TiO_{3} materials possibly displayed the weak ferromagnetism at room temperature. In addition, Hung et al. reported that MgFeO_{3−δ} solid solution in Na_{0.5}Bi_{0.5}TiO_{3} materials exhibited strong magnetic, which were estimated to be around 39.6 memu/g, where the Mg cations played an important role for mediating ferromagnetism. The SrFeO_{3−δ} and CaFeO_{3−δ} modified Na_{0.5}Bi_{0.5}TiO_{3} materials also showed strong enhancement of the magnetization at room temperature. Note that the Mg cations possibly substituted for both A-site (Bi^{3+}, Na^+) and B-site in Na_{0.5}Bi_{0.5}TiO_{3} crystal structure while Sr and Ca cations only replaced with A-site in host Na_{0.5}Bi_{0.5}TiO_{3} crystal structure. Thus, we suggested that the possible room temperature ferromagnetism in BaFeO_{3−δ} modified Na_{0.5}Bi_{0.5}TiO_{3} materials were strongly related to the interaction of Fe cations through oxygen vacancies, like F-central interaction, which were recently suggested for Mn-, Ni-, Co- and Fe-doped Na_{0.5}Bi_{0.5}TiO_{3} materials. A recent X-ray photoelectron spectroscopy (XPS) analysis of CaFeO_{3−δ} modified Na_{0.5}Bi_{0.5}TiO_{3} materials showed that Fe cations are stable in the Fe^{2+} and Fe^{3+} valence state together with O vacancies. Therefore, we suggest that the interaction pair Fe^{2+}−Fe^{3+} favors ferromagnetic ordering. The unsaturation in the M−H curves of magnetic hysteresis loops of Na_{0.5}Bi_{0.5}TiO_{3} materials (under 6 kOe of applied magnetic field) as the amount of the BaFeO_{3−δ} solid solution increase suggested magnetic polaron interaction, wherein the interaction between Fe^{2+}−Fe^{3+} versus Fe^{3+}−Fe^{3+} resulted in antiferromagnetic-like ordering. In addition, isolated Fe cations displayed paramagnetic properties. Thus, the combination of the complex signal of ferromagnetic interaction and antiferromagnetic-like and paramagnetic properties was observed when the BaFeO_{3−δ} solid solution was present at high concentrations in host Na_{0.5}Bi_{0.5}TiO_{3} materials. However, unlike single Fe-doped Na_{0.5}Bi_{0.5}TiO_{3} materials, the modification at A-site (Bi^{3+}, Na^+) via Ba"^{3+} cations in host Na_{0.5}Bi_{0.5}TiO_{3} materials also possibly contributed a source to the ferromagnetic ordering, in which the substitution of Ba"^{2+} cations for Bi"^{3+} cations in crystal structure created the O-vacancies while Ba"^{2+} cations incorporated for Na"^{−} cations generated the Na-vacancies. The role of Na- and O-vacancies are origin of the ferromagnetism, but they work in different ways. Nevertheless, both the experimental observation and theoretical prediction have agreed that Na-vacancies induce the nonzero magnetic moment. Therefore, the strength of magnetic moments can be increased by increasing the number of Na-vacancies. However, unlike Na-vacancies, the O-vacancies were predicted to be agent of the nonmagnetic moment. The O-vacancies were important in promoting the reduction in valence state from Ti^{4+} to Ti^{3+} (even Ti^{2+}) because of oxygen vacancies bounding surrounding. The theory predicted that Ti^{4+} has no magnetic moment whereas the Ti^{3+} or Ti^{2+} have nonzero magnetic moment. Thus, the enhancement of the magnetic moment along with the contribution of magnetization of Ti^{3+}/2+ defects, resulting in increased magnetic moment that were over the self-defects compared with pure Na_{0.5}Bi_{0.5}TiO_{3} samples. Recently, XPS results have shown that the Ti^{4+} cations in Na_{0.5}Bi_{0.5}TiO_{3} materials were possible reduced to Ti^{3+} via modification of CaFeO_{3−δ} and SrMnO_{3−δ} modified as solid solution. Therefore, we suggested that the increasing the O-vacancies was promoted by the magnetization of self-defect of Ti^{4+} cations. Recently, the interaction between Co^{2+}/3+ pair through O-vacancies were suggested to favor the ferromagnetic ordering. Therefore, we suggested that the appearance of interaction Fe^{2+}/3+−Fe^{2+}/3+ pair may arouse increasing of the strength of ferromagnetic ordering. We recently reported that the magnetic properties of various magnetic compound, such as MnO_{2}, Mn_{5}Ge_{3} etc., could be tunable by a strain. Therefore, due to the difference radius with ions of host lattice, the Ba cations could also possibly cause a chemical pressure, resulting in the change of interaction between them through oxygen vacancies; finally, resulted in modification of magnetic ordering strength. Recent experimental and theoretical studies have suggested that transition metals may fill A- and B-sites in the perovskite structure of lead-free ferroelectrics, thus resulting in complex magnetic properties. The Cu modification at the B-site of EuMnO_{3} materials changes magnetic properties from paramagnetic to antiferromagnetic ordering. Deng et al. found that the paramagnetic properties of EuMnO_{3−δ} materials were changed to antiferromagnetic via modification at the Eu site by Mn cations. Magnetic phase transition from paramagnetic to antiferromagnetic properties has also been reported for DyMnO_{3} materials modified with the Mn cation at the Dy-site. Theoretical and experimental studies have suggested that CoTiO_{3} modified Na_{0.5}Bi_{0.5}TiO_{3} materials have complex magnetic properties that are strongly dependent on the location of Co impurities on the A-site or B-site in the host structure. Notably, the radii of Fe^{2+}/3+ cations with VIII coordination are 0.92 Å and 0.78 Å, respectively, which are comparable with the radii of Bi^{3+} (1.17 Å) and Na"^{+} (1.39 Å) cations. Therefore, we suggested that Fe cations were random incorporated at both the A-site and B-site likely contributing to the complex magnetic properties of the host Bi_{3}Na_{0.5}TiO_{3} materials. The role of Fe cation substitution at the A- and B-sites in the magnetic properties of Na_{0.5}Bi_{0.5}TiO_{3} materials was further investigated by using density-functional theory (DFT) calculation. To estimate the origin of the observed ferromagnetism, the density-functional theory (DFT) calculations were performed using the Vienna ab initio Simulation Package (VASP). The generalized gradient approximation (GGA) formulated by Perdew, Burke, and Ernzerhof (PBE) was used for the electron exchange correlation potential. Figure 8a shows the side and top views of the rhombohedral crystal structure of the 24 formula unit (f.u) cell (120-atom) adopted for Bi_{3}Na_{0.5}TiO_{3} (BNT). As model systems shown in Fig. 8b,c, we have considered the substitution of one Ba atom for the Bi-site, denoted as B(Ba)NT, and Na-site [BN(Ba)T], in the 24 f.u. cell structure of the BNT. This corresponds to about 0.83 at.% doping for the A-site (Bi and Na) substitution, which is within the range of the present experimental doping concentrations (0.5–9 mol.%). To represent the presence of the Fe substitution in a sample, we replaced one Ti [BNT(Fe)], Ba [B(Fe)NT], and Na [BN(Fe)T] atom with the Fe atom in the same unit cell, as shown in Fig. 9a–c. For all systems, we used an energy cutoff of 500 eV for the plane-wave basis and a k-point mesh of 5×5×5 for the Brillouin
zone integration. To obtain optimized atomic structures, the atomic positions as well as lattice parameters were fully relaxed until the largest force becomes less than $10^{-2}$ eV/Å and the change in the total energy between two ionic relaxation steps is smaller than $10^{-5}$ eV. Note that the severe distortions of octahedral TiO$_3$ lattice were observed for all geometries after optimization.

We first investigate the energetics of the Ba- and Fe-doped BNT. Here, the formation energy ($H_f$) is defined as $H_f = H - \sum \mu_i n_i$, where $H$ is the total energy of the system, and $\mu_i$ and $n_i$ are the chemical potential and the number of species $i$ in the unit cell. The calculated $H_f$ values of BNT, B(Ba)NT, BN(Ba)T, B(Fe)NT, BN(Fe)T, and BNT(Fe) are shown in Table 1. We find that the $H_f$ of BNT is -2.385 eV/atom, which indicates the pure BNT is quite stable. Our calculations further indicate that the Ba substitute prefers either the Bi or Na sites (A-site), as their enthalpies of formation are competitive (−2.402 and −2.392 eV/atom). The Fe dopant atoms may also occupy both the A- and B-site (Ti), although the absolute values of $H_f$ for the A-site (−2.376 eV/atom for the Bi and −2.355 eV/atom for the Na) are higher than that (−2.335 eV/atom) of the B (Ti)-site in magnitude. Nevertheless, in a real sample, the latter substitution (B-site) might appear more than the A-site (Bi and Na) substitution, as the A-site is mainly occupied by the Ba atoms.

Table 1 shows the calculated magnetic energy ($\Delta E = E_{sp} - E_{non-sp}$, where $E_{sp}$ and $E_{non-sp}$ are the total energies of the spin-polarized and non-spin-polarized states, respectively), total magnetization per f.u. ($M$), and atom
resolved magnetic moment ($m$) of the dopant atoms. Our calculations show that all the Fe-doped structures are magnetic, while the Ba-doped ones are nonmagnetic. The calculated magnetization ranges from 0.14 to 0.21 $\mu_B$/f.u. (or approximately 3.6 to 5.5 emu/g with $[\text{emu/g}] = 1.078 \times 10^{20} (M_{\text{f.u.}}/N_A)$ [$\mu_B$/f.u.], where the $N_A$ and $M_{\text{f.u.}}$ are the Avogadro constant and the molar mass per f.u., respectively) at 0.83 at. % doping. These theoretical magnetization values are much higher than the maximum experimental value of 23 memu/g for 9 mol. % BaFeO$_{3-\delta}$-modified Na$_{0.5}$Bi$_{0.5}$TiO$_3$.

The induced magnetization mainly comes from the local atomic moment of the Fe dopant atoms, as shown in Table 1.

**Figure 10.** Top to bottom: The DFT results of the spin-resolved DOS for the BNT, B(Ba)NT, BN(Ba)T, BNT(Fe), B(Fe)NT, and BN(Fe)T. The Fermi level is set to zero energy.

| $H_f$ (eV/atom) | $\Delta E$ (eV) | $M$ ($\mu_B$/f.u.) | $m$ ($\mu_B$/atom) |
|-----------------|----------------|--------------------|---------------------|
| BNT             | −2.385         | 0                  | 0                   |
| B(Ba)NT         | −2.402         | 0                  | 0                   |
| BN(Ba)T         | −2.392         | 0                  | 0                   |
| B(Fe)NT         | −2.376         | 1.15               | 0.21                | 3.94               |
| BN(Fe)T         | −2.355         | 1.20               | 0.14                | 3.42               |
| BNT(Fe)         | −2.335         | 0.73               | 0.16                | 3.10               |

Table 1. The DFT results of the formation energy $H_f$ (eV/atom), magnetic energy $\Delta E$ (eV/atom), and magnetization $M$ ($\mu_B$/f.u.) of BNT, B(Ba)NT, BN(Ba)T, B(Fe)NT, BN(Fe)T, and BNT(Fe) compounds. We also list the magnetic moment $m$ ($\mu_B$/atom) of the Fe dopant atom for the 1 Fe atom doped 24 f.u. cell of B(Fe)NT, BN(Fe), and BNT(Fe).
n-doped semiconductors, while kept the absolute value of the band gap. On the other hand, as shown in the bottom panels in Fig. 10, for B(Fe)NT, BN(Fe)T, and BNT(Fe), there are some midgap states around the Fermi level. In particular, for BNT(Fe), a finite DOS peak state appears right at the Fermi level in the majority-spin state while the other spin channel exhibits an insulating behavior. This is a feature of the half-metallic electronic nature. Furthermore, for all the Fe-doped compounds, substantially large exchange splitting between the spin subbands (i.e., majority-spin and minority-spin) is prominent (Fig. 10). These peak states are due to the strong orbital hybridization between the Fe 3d and O 2p states. As shown in Fig. 11, the majority-spin bands of the Fe are fully occupied, and the minority-spin states are almost unoccupied for the BNT(Fe) and B(Fe)NT but partially occupied for the BN(Fe)T. Overall, one can expect the large magnetic moment at the Fe site, as addressed in Table 1. Induced moments at the neighboring sites to the Fe are rather small.

Based on the PDOS analyses for the BNT(Fe) and B(Fe)NT compounds, we infer that the six (five) d-orbitals of Fe2+ (Fe3+) ion split by high-spin state through the crystal field theory are filled by the 5 majority-spin electrons in the low-lying t2g orbital levels and 1 electron (no electron) in the minority-spin t2g state. Thus, according to Hund’s rule, the calculated magnetic moments of 4 and 5 μB for the Ti and Bi sites can be explained by the electronic configuration of the high-spin state in the crystal field theory through the unpaired electron spin count. For the BN(Fe)T, the magnetic moment of the Fe atom is reduced compared with those for the other two systems, as some minority-spin states are partially occupied (Fig. 11c). Furthermore, for all compounds, both the t2g and eg states in PDOS are slightly split, which is mainly due to the Jahn–Teller effect as the severe octahedron distortion occurs in the presence of the Fe substitution.

We now investigate the doping concentration dependent magnetization of the Fe and Ba doped BNT. Figure 12 shows the calculated M of BNT(Fe), B(Ba)NT, and BN(Ba)T as function of the concentration of the dopant atoms. Clearly, the magnetization increases linearly from 0.16 μB/f.u. (4.2 emu/g) to 0.66 μB/f.u. (17.3 emu/g) as the Fe concentration increases from 0.83 at.% to 3.33 at.%, as shown in Fig. 12. Our calculated magnetization

![Figure 11.](https://example.com/figure11.png)

**Figure 11.** The DFT results of the d-orbital decomposed PDOS of the Fe substitutional atom for the (a) BNT(Fe), (b) B(Fe)NT, and (c) BN(Fe)T. The black, orange, red, green, and blue lines represent the d_3^2, d_x^2, d_y^2, d_z^2, and d_3xy orbital states, respectively. The Fermi level is set to zero energy.

![Figure 12.](https://example.com/figure12.png)

**Figure 12.** The DFT results of the magnetization (μB/f.u.) of BNT(Fe), B(Ba)NT, and BN(Ba)T as function of the concentration of the dopant atoms.
is much larger than the measured values (23 memu/g at 9 mol.%), which is presumably due to the different concentrations and stoichiometries between the theory (here only the Fe doping) and experiment (Ba and Fe co-doping). Interestingly, the Ba doping for the A-site (Bi and Na) induces magnetism ($M = 0.05 \mu_B/\text{f.u.}$) at about 2.5 at.% (Fig. 12). It is further found that the calculated magnetization increases as the doping concentration increases. Our atom resolved magnetization analyses indicate that the induced magnetization mainly comes from the Ti and O atoms neighboring to the Ba dopant site. The underlying mechanism can be explained by the spin-polarized charge transfer between the dopant and neighboring atoms in the unit cell, as revealed from the Ti- and O-PDOS analyses shown in Fig. 13.

We finally explored the magnetic and electronic properties of the O-vacancy defected BNT(Fe). We have considered the presence of a single vacancy and double vacancies in the Fe-included octahedral cell to imitate different valence states of the Fe dopant atom. Our calculations show that the total magnetization (4 $\mu_B$) of the BNT(Fe) compound decreases by 1 and 2 $\mu_B$ for the single-vacancy and double-vacancy systems, respectively. From the electronic structure analyses shown in Fig. 14a–c, the PDOS of the Fe dopant atom in BNT(Fe) shift toward the low energy region and some minority-spin states are partially occupied in the presences of the single and double oxygen vacancies. This is because of the extra electrons accumulated at the Fe site, originated from

![Figure 13. The DFT results of PDOS of the Ti and O atoms for (a) and (c) (Ba)NT and (b) and (d) BN(Ba)T at 3.33 at.% Ba doping. The Fermi level is set to zero energy.](image)

![Figure 14. The DFT results of the $d$-orbital decomposed PDOS of the Fe substitutional atom for the BNT(Fe) with the (a) vacancy-free, (b) single-vacancy, and (c) double-vacancy. The black, orange, red, green, and blue lines represent the $d_{xy}$, $d_{xz}$, $d_{yz}$, $d_{x^2-y^2}$ orbital states, respectively. The Fermi level is set to zero energy.](image)
the O deficiency in the unit cell. Furthermore, the obtained magnetic moments are simply the reflections of the Fe$^{3+}$ and Fe$^{4+}$ ionic states in the high spin states and mixture of them in a real sample, as addressed in the previous experiment\(^{30}\).

### Conclusion

The solid solution of BaFe$_{0.5-x}$ and Na$_{0.5-3x}$Bi$_{0.5}$TiO$_3$ ceramics have been successfully synthesized by a chemical route and gel method. The Ba and Fe ions were distributed randomly into the Na$_{0.5-3x}$Bi$_{0.5}$TiO$_3$ lattices which caused in the distortion of lattice structure and decreased the optical band gap. The complex magnetic properties were observed in this solid solution. This work shows a simple way for enhancement of room-temperature ferromagnetism in lead-free ferroelectric materials by solid solution.

### Experiment

($1 - x$)Na$_{0.5}$Bi$_{0.5}$TiO$_3$ + $x$BaFe$_{0.5}$ (BNT-xBOF; $x = 0.5\%$, 1\%, 3\%, 5\%, 7\% and 9\%) samples were fabricated by sol–gel method. The raw materials were consisted of Bi(NO$_3$)$_3$, 5H$_2$O, NaNO$_3$, Fe(NO$_3$)$_3$, 9H$_2$O, tetraisopropyltitanium (IV) (C$_{12}$H$_{28}$O$_4$Ti) and BaCO$_3$. The solution was chosen which are acetic acid (CH$_3$COOH) and deionized water with volume ratio of Vi$_{ac}$/V$_{CH_3COOH} = 5:2$ while an acetylacetone (CH$_3$COCH$_2$COCH$_3$) were selected as ligand. First, the BaCO$_3$ was weighted and dissolved under mix acid acetic and deionized water. Thus, the raw materials such Bi(NO$_3$)$_3$, 5H$_2$O, NaNO$_3$, Fe(NO$_3$)$_3$, 9H$_2$O were weighted to add the solution. To following, the solution was added with tetraisopropyltitanium after adding to avoid hydrolysis. The solution was magnetic stirred under several hours to make homogeneous solution of sol. The sol was dried under 100 °C to prepare gels weighed to extra around 40–50 mol% to prevent the sodium evaporation\(^{9–11,24–42,60}\). The crystalline structural of annealing processing that make samples nonstoichiometric composition. Therefore, the sodium nitrate was weighed to extra around 40–50 mol% to prevent the sodium evaporation\(^{9–11,24–42,60}\). The crystalline structural of sol–gel method. The raw materials were consisted of Bi(NO$_3$)$_3$ and BaCO$_3$. The solution was chosen which are acetic acid (CH$_3$COOH) and deionized water with volume ratio of Vi$_{ac}$/V$_{CH_3COOH} = 5:2$.

The solid solution of BaFeO$_{3-\delta}$ and Na$_{0.5}$Bi$_{0.5}$TiO$_3$ ceramics have been successfully synthesized by a chemical route sol–gel method. The Ba and Fe ions were distributed randomly into the Na$_{0.5}$Bi$_{0.5}$TiO$_3$ lattices which caused in the distortion of lattice structure and decreased the optical band gap. The complex magnetic properties were observed in this solid solution. This work shows a simple way for enhancement of room-temperature ferromagnetism in lead-free ferroelectric materials by solid solution.

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D.D. and N.H.L. conceived the idea and designed the experiments. N.H.L., N.A.D., N.N.T., N.V.D., and N.N.T. performed the experiments and measurements. D.O. performed the theoretical calculations and wrote...
the corresponding paragraphs. D.D.D. and N.T.H. wrote the paper. Y.S.K. and A.D.N. reviewed and commented on the paper. All authors discussed the results and commented on the manuscript.

**Competing interests**
The authors declare no competing interests.

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