Hydrothermal synthesis of Ce/Zr co-substituted BiFeO₃: R3c-to-P4mm phase transition and enhanced room temperature ferromagnetism

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Abstract

A facile hydrothermal method was used for fabricating phase-pure Bi₁₋ₓCeₓFe₁₋ₓZrₓO₃ (x = 0.00, 0.03, 0.06) multiferroic ferrites, and the dependence of structural, optical, and magnetic properties on the composition have been investigated. The samples were investigated by X-ray diffraction (XRD), Raman and Fourier-transform infrared (FT-IR) spectroscopies, scanning electron microscopy, UV-Vis spectroscopy, and vibrating sample magnetometer at room temperature. Structural results show that the structure of Bi₁₋ₓCeₓFe₁₋ₓZrₓO₃ ferrites is indexed to a rhombohedral structure with R3c space group. However, the weakening in the intensity, the expansion of the line-width of all bands, and some band shifts observed in Raman spectra indicate a structural transition from rhombohedral (R3c) to pseudo-tetragonal (P4mm) phase as the content of Ce/Zr increases. Also, a significantly enhanced intensity of the A1-2 mode in Raman spectra means that there is a novel behavior of magnetic anisotropy in the Ce/Zr co-substituted samples. A significant increase in optical band gap with increasing of the Ce/Zr co-substitution suggests that the materials are suitable for technological applications. Magnetic properties of the samples show a magnetic transition from antiferromagnetic to ferromagnetic phase due to the presence of the rhombohedral to the tetragonal phase transition, and exchange interaction between the 4f orbitals of the Ce³⁺/Ce⁴⁺ and the 3d orbitals of the Fe³⁺/Fe²⁺.

Keywords: Bismuth ferrite; Hydrothermal method; Structural transition; Raman spectroscopy; Magnetic transition.

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1. Introduction

BiFeO$_3$(BFO) is the most famous multiferroic material having the antiferromagnetic Néel temperature (= 370 K) and the ferroelectric Curie temperature (= 830 K) which simultaneously shows a saturation polarization and magnetic moment of 90 µC/cm$^3$ and 8-9 emu/cm$^3$, respectively [1]. The ferroelectricity and G-type antiferromagnetic characteristics of BFO come respectively from the lone-pair distortion on the 6s$^2$ of Bi$^{3+}$ ions and spin-exchange coupling between half-filled ‘d’ orbital of Fe$^{3+}$ ions [2-3]. Despite this, inherent problems of the bulk BFO such as formation of secondary phases, high leakage current, low magnetoelectric (ME) coupling, zero macroscopic remnant magnetization (M$_r$) have been restricted its multifunctional applications at room temperature [4-7]. In recent years, attempts have been made to enhance reduce dielectric loss, ferroelectric properties, and leakage current, increase remnant polarization, modify its inhomogeneous-spatial spin-modulated (incommensurate) structure, and intensify magnetoelectric interaction [8-21]. However, the comparative studies were undertaken in order to understand of the effect of co-substitution at A- and B-site on ferroelectric and magnetic properties, respectively. Recent studies revealed that a strategy of co-doping of the Bi-site, and Fe-site can significantly improve the magnetic and ferroelectric properties of BFO nanoparticles, [11-21]. We recently reported that the A-site (Nd, Y, Gd) and B-site (Mn, Zr) co-substitution of BFO have a result to reduce the particle size to less than 62 nm which will destruct or suppress the magnetic spiral structure [6-7]. However, in present work, hydrothermal method was used for the synthesis of pure single-phase Bi$_{1-x}$Ce$_x$Fe$_{1-x}$Zr$_x$O$_3$ ($x$ = 0.00, 0.03, 0.06) at a low temperature 180 °C without a further calcination step. Also, we selected Ce substitution, because $r_{\text{Ce}^{3+}}$(CN:12) = 1.34 Å is closer to the $r_{\text{Bi}^{3+}}$(CN: 12) (1.4 Å, 6s lone pair) so that it results in a low symmetry distorted rhombohedral structure with R3c space group accompanied by a large
polarization along the hexagonal [001] or the pseudocubic [111] direction [21-23]. Furthermore, it highly expects that Bi\(^{3+}\) substitution with Ce\(^{3+}\) can reduce the leakage current density accompanied by a further improvement in the ferroelectric properties of BFO [23]. However, Ce\(^{3+}\) substitution act as a donor in oxygen octahedron and helps to reduce the oxygen vacancies by restricting the formation of Fe\(^{3+}\) to Fe\(^{2+}\) ions [21]. Previous reports on Zr\(^{4+}\) substitution for Fe\(^{3+}\) showed that lattice strains and defects originated from a mismatch in ionic radii prevents the growth of the grain sizes as the substitution increases and all the samples show the antiferromagnetic behavior [24]. While in A/Zr co-substitution for Bi/Fe, the particle sizes goes down and a weak ferromagnetic behavior with an improvement of microwaves properties are observed [7, 25]. Detailed studies of structural, optical, and magnetic properties indicate novel behaviors of the pure single-phase Bi\(_{1-x}\)Ce\(_x\)Fe\(_{1-x}\)Zr\(_x\)O\(_3\) (\(x = 0.00, 0.03, 0.06\)) hydrothermally synthesized with improved magnetic properties.

2. Experimental

2.1. Preparation of Bi\(_{1-x}\)Ce\(_x\)Fe\(_{1-x}\)Zr\(_x\)O\(_3\)

To prepare the Bi\(_{1-x}\)Ce\(_x\)Fe\(_{1-x}\)Zr\(_x\)O\(_3\) (\(x = 0.00, 0.03, 0.06\)) nanoparticles by hydrothermal method, first, a solution of initial material nitrates with appropriate moles under continuous stirring is obtained. The Bi(NO\(_3\))\(_3\)5H\(_2\)O is dissolved in 5 mL concentrated HNO\(_3\) and then all ZrO(NO\(_3\))\(_2\)H\(_2\)O, Ce(NO\(_3\))\(_3\)6H\(_2\)O, and Fe(NO\(_3\))\(_3\)9H\(_2\)O were separately dissolved in 5 mL of distilled water. After that, all the precursors were mixed under continuous magnetic stirring to obtain a completely clear solution. Then, 40 g of KOH solution was dropwise added to the above solution and then the mixture was poured into a Teflon-lined stainless steel autoclave for the
hydrothermal treatment at 180 °C for 6 h. The precipitate was filtered and washed with distilled water to remove (NO₃)⁻¹ and K⁺ ions. Next, the resulted precipitate was dried in an oven at 110 °C for 3 h. To ensure accurate and reproducible results, the high purity reagents and chemicals were used which were purchased from Sigma-Aldrich.

The crystal phase of the Bi₁₋ₓCeₓFe₁₋ₓZrₓO₃ (x = 0.00, 0.03, 0.06) nanoparticles was identified by powder X-ray diffraction (XRD, D8-Advance Bruker AXS diffractometer) with a Cu-Kα radiation (λ = 1.54048 Å). The patterns were analyzed by using the Fullprof program. Raman spectra were performed in a Renishaw 1000 confocal Raman microscope using a 532 nm diode-pumped solid-state laser (Cobolt) with a laser power of 10 mW. The Fourier transform infrared (FTIR) spectra of the samples were obtained from a Perkin-Elmer FT-IR spectrometer. The surface morphology images of the samples were recorded by field-emission scanning electron microscopy (FESEM, HITACHI S-4160 model). The absorption spectra of the samples were recorded by a UV-Vis system (Agilent8453, Palo Alto, CA). The direct-transition bandgap energy of the samples was estimated through Tauc’s equation [26]. The hysteresis loops of the samples were recorded using the VSM 7407 Lake Shore's vibrating sample magnetometer at room temperature and a maximum magnetic field of 2T.

3. Results and discussion

3.1. Structural analysis

Fig. 1(a) shows XRD patterns of a single-phase perovskite structure of Bi₁₋ₓCeₓFe₁₋ₓZrₓO₃ (x = 0.00, 0.03, 0.06) nanoparticles. It reveals the presence of a rhombohedral crystal structure with R3c space group for BFO which is in accordance with the JCPDS card (no. 86-1518) [7]. After
Ce\(^{3+}/\text{Zr}^{4+}\) ions doping into BFO, the doublet diffraction peaks (104) and (110), (006) and (202), (116) and (112), (118) and (300) of the rhombohedral structure are merging to the singlet peak as shown in Fig. 1. Also, the location of all the diffraction peaks shifted toward a higher angle.

Although the intensity of XRD peaks located at the higher angles is increasing, the intensity of singlet peak (012)\(_R\) at about 22° becomes smaller. Besides, an enlarged view of (012)\(_R\) and (024)\(_R\) reflections is plotted inset of Fig. 1 to show the structural change as Ce\(^{3+}/\text{Zr}^{4+}\) content increases up to \(x = 0.06\). As seen from Fig. 1, a splitting in both the parallel (012)\(_R\) and (024)\(_R\) reflections of the rhombohedral structure which are singlet peaks, occur with the addition of Ce\(^{3+}/\text{Zr}^{4+}\) content. The singlet (012)\(_R\) peak is split into two sub-peaks, a larger peak at about 22.50° and a smaller peak at about 22.75° which are respectively corresponded to the reflection planes (001)\(_T\) and (100)\(_T\) of tetragonal structure. Similarly, the singlet (024)\(_R\) peak is split into two sub-peaks, a larger peak at about 45.90° and a smaller peak at about 46.40° which are respectively corresponded to the reflection planes (002)\(_T\) and (200)\(_T\) of the tetragonal structure. It should be noted that the intensity of the (001)\(_T\) and (002)\(_T\) reflections of the tetragonal structure is smaller than the (100)\(_T\) and (200)\(_T\), respectively [27]. Since the structure of sample \(x = 0.06\) is a mixture of the tetragonal (\(P4mm\)) and rhombohedral (\(R3c\)) phases, the peak overlap of the (012)\(_R\) with the (001)\(_T\) and the peak overlap of the (024)\(_R\) with the (002)\(_T\) occurs. These findings could be related to the fact that the lower-symmetry rhombohedral structure of BFO gradually transforms into a higher-symmetry tetragonal structure due to the changes of bond lengths Bi-O and Fe-O after the Ce\(^{3+}/\text{Zr}^{4+}\) doping into BFO, which is discussed further below.
Fig. 1 XRD pattern and Rietveld analysis with rhombohedral (space group \(R3c\)) structural model for Bi\(_{1-x}\)Ce\(_x\)Fe\(_{1-x}\)Zr\(_x\)O\(_3\) (\(x = 0.00, 0.03\)) and a mixed-phase tetragonal (\(P4mm\)) + rhombohedral (\(R3c\)) structural models for \(x = 0.06\). Red circles and black solid lines represent the raw data and the calculated profile, respectively. Green vertical lines indicate the position of Bragg peaks for rhombohedral structure. The blue lower trace shows the difference between the observed (the raw data) and the calculated patterns.
Table 1 The lattice parameters of conventional hexagonal \((a_H, c_H)\), primitive rhombohedral \((a_R, a_R)\) structures, crystallite size \((D_{W,H})\) and microstrain \((\varepsilon)\) obtained from the Williamson-Hall method for \(\text{Bi}_{1-x}\text{Ce}_x\text{Fe}_{1-x}\text{Zr}_x\text{O}_3\).

| Sample       | \(x = 0.00\) | \(x = 0.03\) | \(x = 0.06\) |
|--------------|---------------|---------------|---------------|
| \(a_H = b_H\) (Å) | 5.5849        | 5.5691        | 5.5691        |
| \(c_H\) (Å)     | 13.8791       | 13.8384       | 13.8252       |
| \(a_R = b_R = c_R\) (Å) | 5.6394        | 5.6228        | 5.6185        |
| \(\alpha_R = \beta_R = \gamma_R\) (°) | 59.360        | 59.369        | 59.391        |
| \(V_R = V_H/3\) (Å³) | 124.971       | 123.901       | 123.676       |
| \(D_{W,H}\) (nm) | 82.27         | 28.78         | 28.78         |
| \(\varepsilon\) (no unit) | +0.00113      | -5.315E-4     | -5.318E-4     |

Fig. 2 Left panel is a scheme of the relationship between the primitive rhombohedral (dashed, red), cubic (solid, green), and hexagonal cells of bulk BFO. The right panel is half of the left panel. Here, [001] crystallographic axis of the hexagonal structure is parallel to the [111] axis of the rhombohedral or the cubic structures.
The Rietveld refinement of the XRD patterns of the samples using Fullprof software confirms the formation of the rhombohedral structure with \( R3c \) space group (see Fig. 1) and refined lattice parameters listed in Tables 1. Primitive rhombohedral and hexagonal structures in a stable perovskite structure of BiFeO\(_3\) are shown in Fig. 2. The values of the ion radius of the cations used in this work which located at the six-fold coordination site (octahedron site) and the twelve-fold coordination site (dodecahedral site), are as follow: \( r_{Ce^{3+}}(CN: 12) = 1.34 \text{ Å}, \)
\( r_{Ce^{4+}}(CN: 12) = 1.14 \text{ Å}, \)
\( r_{Bi^{3+}}(CN: 12) = 1.4 \text{ Å}, \)
\( r_{Fe^{3+}}(CN: 6) = 0.645 \text{ Å}, \)
\( r_{Zr^{4+}}(CN: 6) = 0.72 \text{ Å} \) [28-29]. According to these values, substituting the smaller \( Ce^{3+} \) for larger \( Bi^{3+} \), will reduce the unit cell volume. Simultaneously, it is expected that \( Zr^{4+} \) replacement instead of \( Fe^{3+} \) will increase the unit cell volume. For better discussion, we calculated the difference in ion radii of the host ions with the substituted ions as follows:

\[
r_{Ce^{3+}} - r_{Bi^{3+}} = -0.06 \text{ Å} \quad \text{and} \quad r_{Zr^{4+}} - r_{Fe^{3+}} = +0.075 \text{ Å}
\]

Therefore, it is expected that the lattice volume will increase with the \( Ce^{3+}/Zr^{4+} \) co-substitution in BFO. However, a shift of the XRD peaks to the larger angles with an accompanying decrease of the lattice volume suggests the presence of various cations of \( Ce^{3+} \) and \( Ce^{4+} \) in the samples (see Table 1). It should be noted that it is harder to enter the \( Zr^{4+} \) ions having an ionic radius larger than \( Fe^{3+} \), which may results in oxidation of \( Ce^{3+} \) to \( Ce^{4+} \). Since the electronic configuration of Ce is \( 4f^1 \ 5d^1 \ 6s^2 \) (atomic number of 58), one among the lanthanides, \( Ce^{3+} \) ions having the configuration \( 4f^1 \ 5d^0 \ 6s^0 \) can easily lose an electron to acquire the configuration \( 4f^0 \) and attains the stable configuration of Xenon. Here, oxidation of \( Ce^{3+} \) (\( Ce^{3+} \rightarrow Ce^{4+} + e^- \)), and reduction of \( Fe^{3+} \) (\( Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \), for the presence of charge neutralization) occur with increase of \( Ce/Zr \) co-substitution, then the oxidation of iron(III) ions by cerium(III) ions results in following relation:

\[
Ce^{3+} + Fe^{3+} \rightleftharpoons Ce^{4+} + Fe^{2+}.
\]
The increase in the angle of $\alpha_R$ near to $60^\circ$ and decreasing of the lattice parameters given in Table 1 with the doping amount of (Ce$^{3+}$-Ce$^{4+}$)/Zr$^{4+}$ ions indicates a slight contraction of the FeO$_6$ octahedral along the body diagonal [111] of rhombohedral (111) axis ($c$ axis of hexagonal) or the c-axis [001], which is accompanied with a transition to a higher symmetry structure (see Fig. 2) [6-7].

In the Williamson-Hall (W-H) method (Fig. 3), the $\beta \cos \theta$ (y-axis) plot versus $4 \sin \theta$ (x-axis) corresponding to the three parallel reflection planes (012), (024), (036) has a positive slope for BFO, while it indicates a negative slope for Ce/Zr co-substituted BFO. The crystallite size ($D$) is calculated by the inverse of the y-intercept of linearly fitted data and microstrain ($\varepsilon$) is obtained from the slope [30]. The results of Table 1 show the remarkable changes in the crystallite size and the microstrain contribution from the broaden X-ray profile for the Ce/Zr co-substituted BFO. With the increase of the Ce/Zr co-substitution in BFO, the value of the $D$ decrease and the $\varepsilon$ become negative due to the presence of compressive stress. This compressive stress created into the BFO lattice can be related to the ionic radii mismatch between Ce$^{3+}$/Ce$^{4+}$ and Zr$^{4+}$ ions with the Bi$^{3+}$ and Fe$^{3+}$, respectively.

![Williamson-Hall plots of Bi$_{1-x}$Ce$_x$Fe$_{1-x}$Zr$_x$O$_3$.](image)

**Fig. 3** Williamson-Hall plots of Bi$_{1-x}$Ce$_x$Fe$_{1-x}$Zr$_x$O$_3$.  

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3.2 Raman and FTIR spectroscopies

Many reasons are indicating that the local structure analysis of substituted BFO nanoparticles can be explained more clearly by the IR and Raman spectroscopies: 1-The structural analysis of BFO nanoparticles by XRD is hampered by the reflection broadening so that splitting the XRD peaks of BFO just covered by the broadening [6]. 2- In particular, the presence of Fe in combination with Cu-Kα radiation leads to significant X-ray fluorescence and high measurement backgrounds [30]. These easily can cover the presence of low-level impurities.

Fig. 4(a) shows the Raman spectra measured at room temperature for Bi$_{1-x}$Ce$_x$Fe$_{1-x}$Zr$_x$O$_3$. According to group theory, distorted rhombohedral BiFeO$_3$ have 18 optical vibration modes (= 4A1+5A2+9E), which A1 (TO) and E (LO) are Raman and infrared active vibration modes, respectively, and 5A2 are Raman inactive vibration modes. So, the 13-point Raman active phonons (= 4A1+9E) of distorted rhombohedral perovskite structure ($R3c$ space group) can propagate in longitudinal and transverse directions as following [31]: Four A1 modes propagating along the c-direction, A1–1, A1–2, A1–3, and A1–4 and nine E modes propagating along the x–y plane. Generally, the A1–1 and A1–2 modes show strong scattering intensities, whereas the A1-3, and A1–4 modes show weak scattering intensities [32-37]. By comparison, the scattering intensity of nine E modes is medium. However, the resonance frequency and the shape of the spectral line depend on the characteristics of the samples. According to previous reports [32-35], the polar phonon modes of A1–1, A1–2, and E1 are mainly contributed to spin-phonon coupling, magnetic anisotropy, and magnetoelectric coupling, respectively. In this research, a slight shift of the A1-1, A1-2, and A1-3 modes (assigned to the Bi–O bonds) to higher
frequencies and a significant change in their intensities with the increase of the Ce and Zr co-substitution indicate that the Ce\(^{4+}\) ions of smaller size are substituted for the Bi\(^{3+}\) ions. Fig. 5 shows two strong peaks near 132, and 168 cm\(^{-1}\) assigned to the A1–1, and A1–2 phonon modes and two weak peaks at 224, and 426 cm\(^{-1}\) assigned to A1–3, and A1–4 phonon modes. Also, the Raman spectra indicate a significant decrease in the scattering intensity of A1-1 mode and an obvious increase in the scattering intensity of A1-2 mode as the Ce/Zr co-substitution increase. The relatively reduced intensity of the A1-1 mode with the degree of the Ce/Zr co-substitution indicates a decrease in the spin-phonon coupling. The relatively enhanced intensity of A1-2 Raman mode with increasing the Ce/Zr co-substitution in BFO indicates that two predominant scattering mechanisms controlling the magnetic anisotropy are the spin-dependent and spin-phonon scattering, so that the Raman intensity of a magnetically ordered phase can be expressed as \(I = |R + M\langle S_iS_j\rangle/S^2|^2\). Here, \(R\) and \(M\) are the spin-independent, and the magnetic moment parameters, respectively, and \(S_iS_j/S^2\) is the nearest-neighbor spin-spin correlation function. The increase in the intensity of A1-2 mode is due to different contributions from the correlation function \(S_iS_j/S^2\), in different directions, which is the result of a change in the magnetic ordering due to the spin-reorientation phase transitions. According to our structural results, it may be attributed to the presence of (001)\(_T\) and (002)\(_T\) peaks oriented in the c-axis direction of the Ce/Zr co-substituted BFO.

The positions of all the observed Raman peaks for samples Bi\(_{1-x}\)Ce\(_x\)Fe\(_{1-x}\)Zr\(_x\)O\(_3\) are given in Table 2. The atomic mass also plays a very important role in a harmonic vibrating system \((\omega = \sqrt{K/m})\). The molar mass of Fe\(^{3+}\), Zr\(^{4+}\), Bi\(^{3+}\), Ce\(^{3+}\), and Ce\(^{4+}\), are 55.845, 91.22, 208.979, 140.114, and 139.905 g/mol, respectively. The molar mass of the Ce\(^{3+}\), and Ce\(^{4+}\) are less than
that of the Bi\(^{3+}\). Nevertheless, at a replacement of less than 15\%, the calculated average molar mass does not have much effect [36].

The Raman spectra (Fig. 4(c)-(d)) show remarkable changes in some band shifts, the expansion of the line-width of all bands, and the weakening in the intensity of the BFO structure with the increases of Ce/Zr content. It indicates an intensity change in \(A_1\) modes and the shift in the \(E\) modes. As seen, the intensity of the \(A_1\)-1 mode decreases, while \(A_1\)-2 phonons increases after Ce/Zr ions are incorporated. When, Ce/Zr co-substitution increases up to 0.06, \(E_4\) mode at 299 cm\(^{-1}\) shifts to a lower wavenumber, followed by merging with the phonon mode \(E_3\) at 263 cm\(^{-1}\). At the same time, the \(E_7\) mode at 471 cm\(^{-1}\) shifts to a higher wavenumber, followed by merging with the phonon mode \(E_8\) at 518 cm\(^{-1}\). According to our structural results, an increase in the intensity of the \(E_7\) mode may be attributed to the presence of peaks \((100)_T\) and \((200)_T\) oriented in an \(a\)-axis direction in the Ce/Zr co-substituted BFO. Also, the \(E_5\) and \(E_6\) modes at 343 and 367 cm\(^{-1}\), respectively, become gradually weak and finally disappear. On the other hand, the mean radius of the Ce\(^{3+}\)/Ce\(^{4+}\) ions is smaller than that of the Bi\(^{3+}\) ions, which a decrease in \(d\) spacing yields a compressive force into the A-sites of the BFO lattice as seen from Fig. 3. These results indicate a structural transition from a rhombohedral structure to a higher-symmetry pseudo-tetragonal, in agreement with our XRD results. When the induced microstrain by the Ce/Zr co-substitution causes the BFO structure to transits to tetragonal \((P4mm\) space group\), the Raman active modes can be expressed by the following irreducible representation: \(3A_1+B_1+4E\) [37].
Fig. 4 (a) Raman spectra (b) FT-IR spectra of Bi$_{1-x}$Ce$_x$Fe$_{1-x}$Zr$_x$O$_3$. Selected enlarged region (200–700 cm$^{-1}$) of samples (c) $x = 0.00$, (d) $x = 0.03$, (e) $x = 0.06$.

Table 2 Raman peak positions for samples Bi$_{1-x}$Ce$_x$Fe$_{1-x}$Zr$_x$O$_3$. The unit is cm$^{-1}$.

| Raman modes (cm$^{-1}$) | $x = 0.00$ | $x = 0.03$ | $x = 0.06$ |
|-------------------------|------------|------------|------------|
| A1-1                    | 132        | 136        | 136        |
| A1-2                    | 163        | 167        | 169        |
| A1-3                    | 218        | 224        | 223        |
| A1-4                    | 428        | 428        | 428        |
| E3                      | 260        | 259        | 252        |
| E4                      | 299        | 270        | 256        |
| E5                      | 337        | 341        | 341        |
| E6                      | 353        | 363        | 363        |
| E7                      | 471        | 482        | 513        |
| E8                      | 518        | 518        | 518        |
Fig. 4(b) shows FT-IR spectrum of Bi₁₋ₓCeₓFe₁₋ₓZrₓO₃ (x = 0.00, 0.03, 0.06). It is known that the absorption frequencies observed in the range of 400 to 700 cm⁻¹ are related to metal-oxygen vibrations of the perovskite structure [38-40]. The strong absorption frequencies found at wavenumbers 475 and 618 cm⁻¹ of the BFO are related to the asymmetric bending and the symmetric stretching vibrations of the iron-oxygen bond in the FeO₆ octahedral iron sites. The former frequency only appears in the high-distortion rhombohedral structure of the perovskite oxides [40]. As seen from Fig. 4(b), there is no absorption peak at about 446 cm⁻¹ for x = 0.06, indicating which a structural phase transition from R3c low-symmetry rhombohedral structure to P4mm high-symmetry tetragonal structure occurs as obtained from XRD and Raman analysis. However, we can observe that the position of absorption peak located at 618 cm⁻¹ shifts to a lower wavenumber located at 558 cm⁻¹, indicating success substitution of the Fe³⁺ ion by bigger Zr⁴⁺ ion.

### 3.3 Morphological analysis

Fig. 5 shows FESEM images for the Bi₁₋ₓCeₓFe₁₋ₓZrₓO₃ (x = 0.00, 0.06) on a scale of 500 nm and 1 µm. The images show the effect of the Ce/Zr co-substitution on the morphology of BFO. The observed micro-and nano-size grains of BFO has a hexagonal basal plane with a nonhomogeneous distribution. It is clear that Ce/Zr co-substitution increases the grain size and the platelet hexagons show lower porosity and higher density than that for BFO. According to the structure results, further reduction in the internal microstrain with increasing the Ce/Zr co-substitution accompanied by a reduction in internal energy and pressure can only be achieved by a decrease of the grain boundary or increase of the grain size [7].
Fig. 5 FE-SEM images for (a), (b) $x = 0.00$, and (c), (d) $x = 0.06$ on a scale of 500 nm and 1 μm.
3.4 Optical characterization

Fig. 6 shows Tauc plots of \((\alpha h\nu)^2\) versus the photon energy \((h\nu)\) of Bi\(_{1-x}\)Ce\(_x\)Fe\(_{1-x}\)Zr\(_x\)O\(_3\) \((x = 0.00, 0.03, 0.06)\). The direct energy gap has been calculated from the extrapolating of the linear part of the plots, as shown in Fig. 6. The bandgap energy of BFO \((\approx 2.04\) eV\)) is related to the electronic charge transfer from O 2p states (valence band) to Fe 3d states (conduction band) which has significantly increased with Ce/Zr co-substitution.

Zhou et al. [41] have reported an increase in optical band gap in Sm and Mn co-doped BFO which may be due to Burstein–Moss effect. A similar increase in optical band gap is also reported for Y and Co co-doping of BFO due to a decrease in the density of state in the valence band [42]. However, there are contradictory reports on the effect of Ce substitution on the bandgap energy of BFO [43-45]. Here, the increase of the gap energy cannot be originated the quantum confinement phenomenon (see the SEM images). It can be attributed to the following reasons: (1) the synergetic effect of Ce and Zr co-substitution on the band structure of BFO is due to the change of the Fe-O and the Bi-O length bonds and the Fe-O-Fe bond angles which may cause a decrease in the density of state in the valence band. (2) According to Burstein–Moss effect, some states close to the conduction band being populated which would result in a blue shift of the optical bandgap, with increasing Ce content (Ce acts as a donor) [7, 41-45]. These will lead to a shift in the fundamental absorption edge towards higher photon energy. A significant increase in optical bandgap energy with increasing of the Ce/Zr co-substitution suggests that the materials are suitable as UV and blue-green-driven photocatalysts, or for optoelectronic devices.
Fig. 6 Plots of $(\alpha h \nu)^2$ vs. $h \nu$ for the samples.
3.5. Magnetic measurements

The room-temperature magnetization curves of Bi$_{1-x}$Ce$_x$Fe$_{1-x}$Zr$_x$O$_3$ ($x = 0.00, 0.03, 0.06$) are shown in Fig. 7. From the curves, we can extract the highest field magnetization ($M_H$), coercive field ($H_c$), magnetization at zero applied fields ($M_r$, the remanent magnetization) for the samples as listed in Table 3.

According to the law of approach to saturation (LAS), anisotropy constant can be calculated by fitting the magnetization curves at the high sufficiently field regions ($H \gg H_c$) with relation (see Fig. 8): $M(H) = M_s \left(1 - \frac{a}{H} - \frac{b}{H^2}\right) + \chi H$, where $M(H)$ is the magnetization at the applied field $H$ [46-48]. Also, the parameters $M_s$, $a$, $b$, and $\chi$ are saturation magnetization, inhomogeneity parameter, factor proportional $K_1^2$ ($K_1$ anisotropy constant), and susceptibility, respectively. They are obtained from the fitting method and listed in Table 3. According to our structural results, the Fe$^{3+}$ ion extracts an electron from Ce$^{3+}$ to form Ce$^{4+}$ and Fe$^{2+}$ ions. However, the Fe$^{2+}$ ion contributes to anisotropy, but the Fe$^{3+}$ ion is expected to be isotropic based on their electron structure. Finally, the increase in the coercive field in Ce/Zr-substituted samples with the substitution has been attributed to the increase of the Fe$^{2+}$/Fe$^{3+}$ ratio and $K_1$ anisotropy constant.

An almost linear increase and small values of the magnetization curves indicate the antiferromagnetic nature of sample BFO which is changed to the weak ferromagnetic as Ce/Zr co-substitution increase (see Fig. 8). However, the presence of the paramagnetic nanoparticles or high magnetic anisotropy of the samples causes the magnetization curves to do not saturate even in the highest applied fields [7, 48]. The increase of $M_r$ and $M_H$ with the Ce/Zr substitution can be related to two reasons: First, a mixture of the rhombohedral and tetragonal
structural phases can destroy the spiral spin modulation with an increase of the magnetization [6-7, 49-50]. Second, when magnetic ion Ce$^{3+}$ having a large magnetic moment of 2.4 $\mu_B$ substitutes for nonmagnetic ion Bi$^{3+}$, an exchange interaction between 3d orbital of Fe$^{3+}$ ion and 4f orbital of Ce$^{3+}$ ion at the B- and A-sites, respectively, produce a local ferrimagnetic spin configuration accompanied by a magnetic enhancement [51].

![Magnetization curve measured at 300 K for Bi$_{1-x}$Ce$_x$Fe$_{1-x}$Zr$_x$O$_3$.](image)

**Fig. 7** Magnetization curve measured at 300 K for Bi$_{1-x}$Ce$_x$Fe$_{1-x}$Zr$_x$O$_3$.

![LAS curves for Bi$_{1-x}$Ce$_x$Fe$_{1-x}$Zr$_x$O$_3$.](image)

**Fig. 8** LAS curves for Bi$_{1-x}$Ce$_x$Fe$_{1-x}$Zr$_x$O$_3$. 
Table 3: The values of remanent magnetization ($M_r$), coercivity ($H_c$), and magnetization at the highest applied field ($M_H$) and the fitting parameters of LAS curve ($M = M_s(1-\alpha/H-\beta/H^2)+\chi H$) for Bi_{1-x}Ce_xFe_{1-x}Zr_xO_3.

| Sample | $H_c$ (Oe) | $M_H$ (emu/g) at 2T | $M_r$ (emu/g) | $a$ (Oe) | $b\times10^6$ (Oe²) | $\chi\times10^5$ (emu/Oe) |
|--------|------------|---------------------|---------------|----------|---------------------|--------------------------|
| $x = 0.00$ | 2.56       | 0.427               | 0.96 E-4      | 2975.78  | 2.93                | 1.38                     |
| $x = 0.03$ | 6.50       | 0.634               | 5.23 E-4      | 2738.87  | 2.62                | 1.86                     |
| $x = 0.06$ | 7.10       | 0.784               | 5.31 E-4      | 3154.20  | 3.18                | 2.41                     |

4. Summary

We have summarized the key points from our work on the Ce/Zr co-substituted BFO as follows: (1) the XRD and Raman spectroscopy results indicate a rhombohedral-tetragonal phase structural transition. (2) The lattice distortion observed in Ce/Zr co-substituted BFO accompanied by the anomalous enhancement of the A1-2 mode induces a magnetic anisotropy in BiFeO₃. (3) Increasing the Ce/Zr co-substitution decreases the values of crystalline size due to the increase of the compressive stress induced into the BiFeO₃ lattice, while it increases the particle size. (4) The bandgap energy significantly increases with the increasing of Ce/Zr co-substitution suggesting that the materials are suitable as UV and blue-green-driven photocatalysts, or for optoelectronic devices. (5) The weak ferromagnetic behavior observed in Ce/Zr co-substituted samples is related to the following reasons: the destruction of a cycloidal antiferromagnetic structure of BFO due to the rhombohedral-tetragonal structural transition, and the exchange interaction between the 4f- and 3d magnetic orbitals of Ce³⁺ and Fe³⁺ ions.
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