Structural evolution induced by acceptor doping into BaTiO$_3$ ceramics

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Solid state reaction method is used to synthesize Ba(Ti$_{1-x}$TM$_x$)$_3$O$_{12-δ}$ (TM = Fe, Mn and Co) and (Ba$_{1-y}$Sr$_y$)(Ti$_{1/3}$Fe$_{2/3}$)$_3$O$_{12-δ}$ ceramics. The X-ray diffraction, scanning electron microscopy and transmission electron microscopy investigations reveal that structural evolutions from an orthorhombic BaTiO$_3$ to a hexagonal Ba(Ti$_{1-x}$TM$_x$)$_3$O$_{12-δ}$, a hexagonal to a rhombohedral in Ba(Ti$_{1-x}$Mn$_y$)$_3$O$_{12-δ}$, and a hexagonal to a pseudo-cubic transition in (Ba$_{1-y}$Sr$_y$)(Ti$_{1/3}$Fe$_{2/3}$)$_3$O$_{12-δ}$ are induced by increasing the doping concentration. Due to the oxygen vacancies derived from acceptor doping, nanoscale domains of incommensurate modulation (ICM) resultant are commonly observed in the hexagonal Ba(Ti$_{1-x}$TM$_x$)$_3$O$_{12-δ}$ compounds. The newly discovered rhombohedral Ba(Ti$_{1/3}$Mn$_{2/3}$)$_3$O$_{12-δ}$ having characteristic of face-sharing prism corner-connected by oxygen atoms is a typical example in searching for novel multiferroics. Discrepancies between the ionic radii of the B- and A-site dopants and that of Ti and Ba as a function of the doping concentrations, i.e., the effects of oxygen vacancies and the electronic configurations of the dopants, are concluded to be the driving forces for the structural transitions.

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1. Introduction

The magnetoelectric multiferroics, in which the ferromagnetism and ferroelectricity coexist, is becoming more and more attractive in recent years because of the potential applications in multiple state memory elements, magnetic valve, filtering device, etc. [1, 2]. In spite that many magnetoelectrics with strong coupling interactions have been discovered, BiFeO$_3$ is the unique single-phase magnetoelectrics with ferroelectric Curie temperature (∼820°C) and antiferromagnetic Neél temperature (∼370°C) above room temperature [3]. As an alternative attempt to search for room temperature magnetoelectrics, the substitution of B-site d$^0$ cations in ferroelectric perovskite oxides by magnetic d$^1$ cations was revitalized recently. Take Ba(Ti$_{1-x}$Fe$_x$)$_3$O$_{12-δ}$ as an example, coexistence of room temperature ferroelectricity and ferromagnetism was revealed in a tetragonal polymorph [4–6]. Room temperature ferromagnetism was also realized in the transition-metal doped hexagonal polymorph [7–10].

As an effective approach in altering or modifying physical properties, doping into ABO$_3$ compounds at A-site or B-site is widely used. Recent investigations on the microstructure and magnetic properties of K/Sr and Fe codoped BaTiO$_3$ reveal that room temperature ferromagnetism was achieved by annealing [11, 12]. This means that transition-metal doped (Ba$_{1-x}$Sr$_x$)TiO$_3$ (BST), which has been one of the most promising materials for practical use in the capacitor of gigabit dynamic random access memories [13], will be good candidates for multiferroic research. Furthermore, enhanced ferroelectric properties of Fe-doped BaTiO$_3$ thin film are also reported in Ref. [14]. It should be noted that the variations of electronic structure of the host elements induced by the dopants will play a dominant role in the magnetic and ferroelectric behaviors of the doped system. The giant dielectric permittivity observed in Li and Ti doped NiO is a good example [15].

Meanwhile, structural phase transition caused by doping will help us to synthesize new compounds, whose room temperature magnetoelectric effect can be expected owing to the novel physical properties and the origin mechanisms of the ferroic orders. As the ferroelectricity revealed in DyMn$_2$O$_5$ [16] and YMnO$_3$ [17], in which the asymmetric pyramidal coordination plays an important role, the control of the oxygen vacancy location may bring about the varied coordination and subsequently the possible novel multiferroics [18]. In view of the situations mentioned above, by means of replacing Ti by Fe, Mn and Co in BaTiO$_3$ and Sr doping into A-site of Ba(Ti$_{1/3}$Fe$_{2/3}$)$_3$O$_{12-δ}$, new compounds are explored in the form of structural evolution in this paper. In addition to the nanoscale domains coming from structural incommensurate modulation (ICM) in the 6H-type compounds, rhombohedral Ba(Ti$_{1/3}$Mn$_{2/3}$)$_3$O$_{12-δ}$ (isostructural to BaFeO$_3$ with a space group of...
R-3m) characterized by face-sharing prism corner-connected by oxygen atoms is discovered. As the structural evolution from the tetragonal to the hexagonal revealed in transition-metal doped BaTiO₃ [10,19] and Sr-doped Ba(Ti₁₋ₓFeₓ)O₃ [20], the reason for the stabilization of the hexagonal phase due to acceptor doping is discussed.

2. Experimental details

Samples were prepared with traditional solid state reaction method from stoichiometric quantities of carbonates and oxides of the different constituents according to the general formula (BaₓSrₓ)₃Ti₄O₁₂, where TM = Fe, Mn and Co. The Sr was merely doped into Ba(Ti₁₋ₓFeₓ)O₃ in which the ratio of B-site Ti/Fe was fixed at 1/2. The BaCO₃, TiO₂, Mn₂O₃ and Co₂O₃ with purities of ≥99.0% as well as Fe₂O₃ (≥99.99%) were used in our experiments. High purity BaCO₃ and TiO₂ (≥99.99%) were used in Fe-doped case in order to figure out the purity influence to the poly-

X-ray diffraction (XRD) experiments were carried out on Philips X’Pert PRO powder diffractometer (Cu Kα = 1.5406 Å) with a scan step of 0.017, and the data refinement was performed with Rietveld method on FullProf software package. An XL30 S-PEG scanning electron microscope (SEM) (FEI) with an accelerating voltage of 10kV and a transmission electron microscope (TEM) equipped with a field emission gun operated at 200kV were used to characterize their morphology and structure, respectively. Specimens for TEM observations were prepared by mechanically polishing then ion milling or crushing the sample in ethanol into fine fragments then supporting them on carbon film covered copper grid.

3. Results

3.1. Orthorhombic to hexagonal transition in Ba(TiₓFe₁₋ₓ)O₃ ceramics

Fig. 1(a) and (b) shows the schematic crystal structures of orthorhombic BaTiO₃ (o-BT) and 6H-hexagonal BaTiO₃ (h-BT), respectively. In order to figure out the doping limit and in consideration of the B-site atom ratio M₂/M₁ = 2 (M₁ and M₂ are two different occupations at B-site in the 6H polymorph) in the hexagonal phase, x = 0, 1/18, 1/10, 1/6, 1/3, 2/3 and 9/10 are chosen in Ba(Ti₁₋ₓFeₓ)O₃, which are abbreviated as BT, BTF05, BTF10, BTF17, BTF33, BTF67, BTF90, respectively, and the XRD patterns are shown in Fig. 1(c). The BT forms an orthorhombic phase (α ≈ 4.02(6), b ≈ 4.00(6) and c ≈ 3.95(6) Å; α = β = γ = 90°) (space group Ammm), and a pure hexagonal polymorph (space group P6₃/mmc) is obtained when 1/10 Fe is doped. The pure hexagonal phase is not acquired in x = 1/18 doped BT matrix in our experiments. Studies on doping limit in BaTiO₃ were also performed by other groups [21,22]. As Fig. 1(d) exhibits, post-annealing in air does not eliminate the coexisted rhombohedral phase. The BTF05 synthesized with high purity reactants highlights increase of the amount of the secondary phase. It is concluded that the adaptable doping range is from 1/10 to 7/10 [22,23], nevertheless, amount of chemical bond breaking induced by high concentration of acceptor incorporation substantially alters the microscopic structure of the doping system. Furthermore, the general expansion of cell parameters in the oxygen vacancy abundant hexagonal phases [21,24] seems to be failed in our experiments (see Fig. 1(c)). Details on these two points will be discussed later. The stable bulk hexagonal compound with x = 1/2 is almost absent, but Grey et al. [21] reported a sub-stable phase obtained by quenching the sample in liquid nitrogen or slow cooling it in oxygen atmosphere.

When doping concentrations get close to the high concentration limit, a secondary phase isostructural with an orthorhombic BaFe₂O₄ [9] often occurs, as the peak at 2θ ≈ 28.3° denoted on BTF67 and BTF90 in Fig. 1(c). Post-annealing in air at high temperature, e.g., 1100 °C, is an effective approach to avoid it. In order to offset the excessive chemical imbalance, tetravalent Fe usually comes into being when doping concentration becomes higher than x = 8/10 [6,21]. In this high doping region, temperature, atmosphere and even humidity, etc. are crucial factors in getting the expected polymorph [21,22,25]. Take BTF90 for example, the hexagonal phase is obtained at the sintering temperature of 1300 °C (20h × 2) in air while a monoclinic phase (α ≈ 6.92(9), b ≈ 4.89(8), c ≈ 2.82(2) Å, α = γ = 90° and β = 90.3°) is acquired when sintering is carried out with successive annealing from 1100 °C (48h) to 800 °C (48h) in air, then to 650 °C (48h) in oxygen atmosphere (see Fig. 1(e)) [25]. The reported powder neutron diffraction, the refinement of XRD data and mössbauer study for h-Ba(TiₓFe₁₋ₓ)O₃ suggest that oxygen vacancy merely locates at O(1) randomly [21,26–28]; even in BaFe₂O₄ [29], the vacancy content at the hexagonally stacked AO₃ layers is more than that at the cubic stacked layers. However, structural phase separation deriving from both O(1) and O(2) vacancies is identified in our experiments. As the morphology of as-prepared BTF17 exhibited in Fig. 2(a), two kinds of equivalent amount of grains shaped in particles (<1 μm) and sheets (~10 μm
Fig. 2. (a and b) The SEM morphologies of the as-prepared and the post air-annealed BTF17, respectively. (c and d) The ED patterns of the as-prepared BTF17 taken along [0 0 1] zone axis. (e) The corresponding HRTEM image of (c). (f) The corresponding HRTEM image of (d), showing $\lambda = 1.66$ nm, $\alpha \approx 27.02^\circ$ and $S \approx 9$ nm.

In the as-prepared sample, two kinds of structures differentiated from electron diffraction (ED) patterns along [0 0 1] zone axis and related high-resolution TEM images are correspondingly observed. Fig. 2(c) and (e) shows the non-modulated phase (NMP), which preserves the six-fold symmetry characteristics of h-BaTiO$_3$. It should be noted that in the hexagonal compounds with $x < 1/6$, such as BTF10, its structure possesses the non-modulated condition and the vacancy is confined at O(1) only (see Table 1).

Fig. 2(e) and (f) shows the counterbalanced modulated phase (MP), an ICM in the $(0 0 1)^*$ plane is featured by modulation wavelength $\lambda$, tilting angle $\alpha$ (relative to reciprocal vector $g_{[1 1 0]}$) and domain size $S$ (the distance in real space derived from the splitting
Fig. 3. (a) The XRD patterns of BSTF05, BSTF11, BSTF17, BSTF33, BSTF50, BSTF67 and STF, respectively. The intensity variations of the peaks denoted by the stars in BSTF11 and BSTF17 suggest an enhanced content of the rhombohedral phase in the parent hexagonal polymorph. (b–e) The morphologies of BSTF33, BSTF50, BSTF67 and STF, respectively; their prototype structure SrTiO₃ (space group Pm-3m) is inserted in (a). (f and g) The ED patterns of BSTF67 along [1 0 0] and [1 1 1] zone axes, exhibiting a pseudo-cubic phase.

satellite spots), which is comparable to a characteristic collective pinning length \( L_c \) \cite{30,31}. Post-annealed BTF17 exhibits a uniform ICM, and the XRD refinement suggests that O(2) vacancy simultaneously comes into being associated with the O(1) vacancy (see Table 1). When \( x \geq 1/3 \), our statistical TEM experiments reveal that the content of NMP decreases sharply and is even negligible as we observed in the as-prepared BTF33 and BTF67, post-annealing in air can effectively purify the phase separated compounds to be a pure MP, as that happened to BTF17. Therefore, in contrast to the corner-connecting polyhedra in or-BT, the face-sharing octahedra come into being in Fe-doped hexagonal compound, as the schematic crystal structures of o-BT and h-BT shown in Fig. 1(a) and (b). When \( x < 1/6 \) is doped, the transition from face-sharing to edge-sharing is generated due to O(1) vacancy only, as the case
occurred to BTF10. Further Fe doping \((x \geq 1/6)\) causes the simultaneous appearances of O(1) and O(2) vacancies and subsequently the amount of bond breaking, as the structural phase separation revealed in BTF17. Correspondingly, the connecting approaches of the polyhedra in hexagonal BTF90 change to point connecting in monoclinic BTF90.

### 3.2. Hexagonal to pseudo-cubic transition in \((\text{Ba}_{1-x}\text{Sr}_y)(\text{Ti}_{1/3}\text{Fe}_{2/3})\text{O}_3\) ceramics

Fig. 3(a) shows the XRD patterns of post-annealed \((\text{Ba}_{1-x}\text{Sr}_y)(\text{Ti}_{1/3}\text{Fe}_{2/3})\text{O}_3\) with doping concentrations of \(y = 1/18, 1/9, 1/6, 1/3, 2/3, 1, \) which are abbreviated as BSTF05, BSTF11, BSTF17, BSTF33, BSTF50, BSTF67 and STF, respectively. Being similar to BTF67, BSTF05 exhibits a pure hexagonal phase. When doping reaches \(x = 1/9\) (BSTF11) and 1/6 (BSTF17), the content of the secondary rhombohedral phase increases in the parent hexagonal phase. Subsequently, when \(x \geq 1/3\), pure perovskite structures with pseudo-cubic polymorph \((a \approx b \approx c \approx 3.96(9), 3.94(3), 3.92(3)\) and 3.88(6) Å; \(\alpha \approx \beta \approx \gamma \approx 90°\)) for BSTF33, BSTF50, BSTF67 and STF, respectively) are obtained[18,20]. The connecting way between the polyhedra thoroughly transforms into corner sharing in comparison with that in hexagonal BSTF05. The decrease of the cell parameters is seen from the shift of the peaks to higher 2\(\theta\) values (see Fig. 3(a)). Fig. 3(b)–(e) shows the morphology of the latter four samples, the grain size increases from ∼2 to ∼6 μm with increasing doping content. However, when Ba is completely substituted, powder-like fragile particles (∼1 μm) possibly resulted from amount of oxygen vacancies and B-site ion mismatch are obtained in STF. As a representative illustration, the ED patterns along [1 0 0] and [1 1 1] zone axes of the pseudo-cubic phase in BSTF67 are presented in Fig. 3(f) and (g), respectively.

### 3.3. Hexagonal to rhombohedral transition in \(
\text{Ba(Ti}_{1-x}\text{Mn}_x)\text{O}_3\) ceramics

As an adjacent transition-metal element of Fe, Mn is also doped into BaTiO\(_3\) to search for novel multiferroic systems. Hexagonal phases are also obtained in \(
\text{Ba(Ti}_{1-x}\text{Mn}_x)\text{O}_3\)
when \(x\) ranges from 1/18 to 1/3 (see Fig. 4(b)). For the Mn-doped case, the stabilization of the hexagonal phase with respect to the doping concentration was discussed a lot [23,32,33], and the reported least amount was \(x = 2/100\) Mn\(^{4+}\) [32] (the Shannon ionic radii (IR) [34] are listed in Table 2). In our experiments, the sensitivity of a pure hexagonal phase to valance state is also verified. As depicted in Fig. 4(c), a tetragonal phase as a secondary phase evidently occurs in the post-annealed BTM05. In spite that the as-prepared one is not pure, the preliminary oxidized Mn\(^{3+}\) in O\(_2\) atmosphere, in which partial Mn\(^{4+}\) comes into being, reduces the content of the secondary phase greatly. The rhombohedral phase becomes counterbalanced in BTM05 sintered in N\(_2\) atmosphere, in which the content of Mn\(^{3+}\) is dominant. Thus, the valence state of doped Mn ion plays a crucial role in the formation of hexagonal phase. As we observed in BTF17, TEM experiments reveal that the hexagonal BTM05 and BTM11 are both structurally separated and post-annealing in air can effectively purify the compound to be a uniform MP. When doping concen-
tation increases to \( x = 1/3 \), a rhombohedral phase is generated in BTM33 (see Fig. 4(b)). Nevertheless, BTM67 shows a pure rhombohedral phase (\( a = b = 5.68(1) \) Å, \( c = 27.85(4) \) Å; \( \alpha = \beta = 90^\circ, \gamma = 120^\circ \)), which is isostructural with BaFeO\(_3\) (Space group R-3m). The coordination of Ti and Mn has changed from the vacancies co-occupied at O(1) and O(2) in h-BTM17 to face-sharing prismatic and corner-connecting polyhedra (see Fig. 4(a)). The strongest peak has been altered because of the co-occupation of Ti and Mn ions at B-site (see Fig. 4(d)). The morphology of the as-prepared BTM67 with grain size of 1–3 \( \mu \)m (see Fig. 4(e)) suggests that BTM67 is a uniform phase, and the ED patterns along [0 1 0], [1 1 0] and [0 0 1] zone axes of the rhombohedral structure are shown in Fig. 4(f)–(h).

3.4. Orthorhombic to hexagonal transition in Ba(Ti\(_{1-x}\)Co\(_x\))O\(_3\)–\(\delta\) ceramics

As another adjacent transition-metal element of Fe, Co is also doped into BaTiO\(_3\). For the substitution of Ti by Co at B-site [19], the doping concentration in hexagonal phase reported by Keith et al. [23] is no more than \( x = 1/10 \). However, \( x = 1/3 \) doping is successfully realized in the hexagonal polymorph when sintering is carried out at lower temperature in our experiments. Fig. 5(a) shows the XRD patterns of BTC10 (\( x = 1/10 \)) and BTC33 (\( x = 1/3 \)). The TEM investigations reveal that both BTC10 and BTC33 have a pure MP. Fig. 5(b) and (c) shows the morphology and the [0 0 1] zone axis high-resolution TEM (HRTEM) image of BTC33, respectively. It is found that the sample is crystallized loosely, the ICM depicts the modulation wavelength \( \lambda \approx 1.26 \) nm and domain size \( S \approx 4.1 \) nm.

4. Discussion

Generally speaking, the structural transition from the orthorhombic to the hexagonal is observed in BaFeO\(_3\), Mn and Co doped BaTiO\(_3\). Apart from the different acceptor doping ranges in stabilizing the hexagonal phase at room temperature, among which Fe could be doped most, structural ICM caused by O(1) and O(2) vacancies prevails in the hexagonal system. In spite that the bond breaking will possibly reduce the long-range ferromagnetic interaction, new types of magnetic interactions and the probable relaxor ferroelectricity could be expected due to the nanoscale structural modulation. As the magnetocapacitive coupling revealed in relaxor ferroelectricity and ferromagnetism coexisting CdCr\(_2\)S\(_4\) [35], in which the ferroic orders develop independently, novel room temperature multiferroics could be expected.

Meanwhile, owing to the oxygen vacancies introduced by acceptor doping, the varied coordination environment of the transition metals may be quite important. As the structural features revealed in multiferroic DyMn\(_2\)O\(_5\) [16] and YMnO\(_3\) [17], the pentahedral Mn\(^{3+}\)O\(_5\) units determine the ferroelectricity of the two compounds. Similarly, ferroelectricity may also be observed in anisotropic BTF10 due to the edge-sharing pentahedra. Being different from the coordination in the multiferroic perovskites [36] and the above-mentioned hexagonal polymorphs, the compound BTM67 characterized by face-sharing prism connected by corner oxygen atoms is newly discovered, possibly, novel multiferroic behaviors will be presented.

As for the stabilization of the hexagonal phase influenced by transition-metal doping, factors such as (i) oxygen vacancies, (ii) the electronic configuration of the dopant ion, (iii) metal–metal bonding of cations through the face-sharing octahedra, (iv) the tolerance factor \( t = (r_A + r_O)/\sqrt{2(r_B + r_O)} \), as well as (v) the Ba/Ti ratio are discussed [23,32,37]. First of all, for the non-doped BaTiO\(_3\), the oxygen-deficient h-Ba(Ti\(_{1-x}\)Fe\(_x\))O\(_3\)–\(\delta\) obtained by reducing the tetragonal polymorph [38] suggests the simultaneous appearances of oxygen vacancies and partial Ti\(^{3+}\), i.e., one O(1) vacancy in the h-BaO\(_3\) layers causes the transformation from face-sharing octahedra to edge-sharing pentahedra, and the appearance of Ti\(^{3+}\) due to the electro-neutral requirement can be well accommodated in the varied coordination environment regardless of the slight increase in the IR of Ti\(^{3+}\). This case is observed in BTF10 (see Tables 1 and 2).

Second, the substitution concentration of Fe\(^{3+}\), Mn\(^{3+}\) and Co\(^{3+}\) is qualitatively determined by their size differences from the average IR of Ti\(^{4+}\) and Ti\(^{3+}\). The IR of the dopants is severely impacted by the initial synthesis conditions as we observed in BTF05 and BTM05. The existence and contribution of Ti\(^{3+}\) have rarely been reported and discussed before [4,8,9,21,23,33]. However, this plays an important role in the magnetic and electrical behaviors of the doping system. Generally speaking, the IR of the incorporated trivalent ions is smaller than that of Ti\(^{4+}\), even Ti\(^{3+}\), when doping concentration becomes high, the existence of the larger size Ti\(^{3+}\) seems to be necessary to hold the hexagonal polymorph. This is consistent with the results of our XRD refinement, where fractional Ti\(^{3+}\) usually plays a crucial role in lowering the \( R \) values in refinements. Detailed electron energy loss spectrum analysis is in progress. In addition, the structural transitions from the hexagonal to the rhombohedral in Mn-doped case and the hexagonal to the pseudo-cubic in Sr-doped BTF67 demonstrate the dominant role of smaller sizes of the dopants at both A- and B-site in driving the structural transformation.

Fig. 6 shows the doping concentration dependence of \( a \) and \( c \) in post-annealed Ba(Ti\(_{1-x}\)Fe\(_x\))O\(_3\)–\(\delta\) ceramics, a slight contraction of the parameters occurs in contrast to the as-prepared ones. The parameter \( a \) generally shrinks with increasing \( x \) in our experiments, while the expansion of \( a \) extends to \( x = 2/3 \) then drops in quenched samples [21]. The maximum of \( c \) occurs at \( x = 1/3 \) compared to \( x = 2/3 \) reported by Grey et al. [21]. Combining with the structural evolutions induced by A- and B-site substitution, from the obtained results we suggest that the effect of metal–metal bonding impacted greatly to the quenched samples [21] is not prominent in our experiments. Additionally, the ICM which possibly does not exist in the quenched samples may be another reason for the discrepancies.
a word, the discrepancies between our results and those reported by Grey et al. [21] may be caused by the different synthesis conditions. The structural phase separation may be caused by O(1) and O(2) vacancies and the smaller ion substitution while the contribution of metal–metal bonding is negligible. This is reflected from the structural characteristics of BTF10, BTM11 and BTC10. Therefore, a much wider doping range can be accommodated when the size of the dopant is much closer to Ti ions.

The preparation conditions are merely used to adjust the electronic structure of the dopants and such an effect is prominently manifested in BTF90 where two kinds of polymorphs are obtained when two sintering routes are carried out. The structure evolution from the hexagonal to the monoclinic is greatly affected by the ratio of Fe⁴⁺/Fe³⁺ because a much smaller IR can be expected on Fe⁴⁺ and the structural stability is well compensated when less oxygen vacancies appear. The reported versatile polymorphs of BaFeO₃₋₁ and BaMnO₃ and BaCoO₃₋₁ demonstrate that the IR and the associated electronic structure of the transition metals play determinant roles in phase identification. However, the tolerance factor seems failed in leveling the expected polymorphs with amounts of oxygen vacancies.

5. Conclusions

Structural transitions from an orthorhombic to a hexagonal phase are all observed in Fe, Mn and Co doped BaTiO₃ systems with starting concentrations of ∼1/10. Transitions from a hexagonal to a rhombohedral phase in Ba(Ti₁₋ₓMnx)O₃₋₁ and a hexagonal to a pseudo-cubic phase in (Ba₁₋ₓSrx)(Ti₁/3Fe₂/₃)O₃₋₁ are observed as well. The solubility of the doped metals in BaTiO₃ is strongly dependent on the preparation conditions, as we observed in BTF05, BTM05, BTF90 and BTC33. Oxygen vacancies at both O(1) and O(2) as well as the substitution of smaller cations at B-site result in an incommensurate modulation in the hexagonal polymorph, which causes a structural phase separation in Fe-doped cases. The size effect of dopants in B-site doped compounds such as BTF10, BTM1 and BTC10 and A-site substituted BTF67 further verifies the influence of ionic radii to structural evolution.

In summary, the oxygen vacancies, smaller cation substitutions of A-site Ba and B-site Ti and thus related electronic configuration variations of elements in the doped matrix are the fundamental driving forces for the structural evolutions. Different coordination of the B-site cations centered polyhedra is obtained in the acceptor doped BaTiO₃ system. Detailed investigations on the physical properties of these samples are undergoing.

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