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Special Topics

Hyper-Ordered Structures: Recent Progress and Future Perspectives

Hyper-Ordered Structures in Dielectric Materials

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Hyper-ordered structures (HOSs) form through a synergy between local imperfections like defects or impurities and a surrounding environment around them, to give rise to emergent functionalities that can never be obtained with the local structures or homogeneous bulk materials alone. Typical examples are ensembles of heterovalent ionic substituents and the related ionic vacancies for charge compensation. Enhanced properties are often electrical in nature, such as improved permittivity, breakdown strength, and energy storage efficiency. In this work we overview HOSs in ferroelectric and dielectric materials from conventional to newly proposed ones and discuss their potential to design innovative next-generation materials for dielectric and energy storage applications.

1. Introduction

Dielectric materials are key ingredients for modern electronics along with magnetic materials and semiconductors. Considerable efforts have been devoted so far to increase the permittivity of dielectric materials, aiming for miniaturizing electronic devices and the development of high-density energy storage devices.¹⁻⁶⁾ There are several conventional approaches to design the permittivity of materials: the additivity rule of polarizability is applied for materials with the permittivity ε' of the order of $10^{0}-10^{1.7}$ Ferroelectric phase transitions have been used to develop large permittivity materials displaying ε' values greater than 10³ like BaTiO₃.⁸⁾ The spatial heterogeneity of electric properties in polycrystalline materials or at sampleelectrode interfaces often gives apparently huge permittivity $\varepsilon' > 10^4$ as widely known as the Maxwell–Wagner–Sillers effect.9-12)

In this review, we introduce hyper-ordered structures (HOSs) as a useful concept for engineering functional properties of the dielectric materials by referring to recent experimental and theoretical findings. HOSs are extended defect complexes with emergent functionalities to improve bulk properties, which form through interactions between local imperfections and the surrounding matrix. In this respect, polar nanoregions (PNR) in relaxors can be regarded as a conventional example of HOSs in dielectric materials. Recent developments in experimental techniques like pair distribution function analyses, transmission electron microscopy, and x-ray fluorescence holography pave the way for direct measurements of HOSs in dielectric materials.¹³⁻¹⁶⁾ This technical advance would provide a fresh insight not only into conventional HOSs like PNR, but also into new ones such as the so-called electron-pinned defect-dipoles (EPDDs), which are a special defect complex that markedly enhances dielectric properties of paraelectric materials. 17

In the second section, we will overview HOSs in relaxors and related ferroelectrics from a viewpoint of functionality for energy storage ceramics. The third section touches upon the EPDDs in modified rutile-type TiO_2 , which has recently been proposed as a novel concept for permittivity boosting. Discussions in these sections are briefly summarized in the final section.



Fig. 1. (Color online) Polarization–electric field (P-E) loop for a dielectric capacitor. E_{max} refers to the maximum applicable electric field, i.e., the dielectric breakdown strength.

2. Hyper-Ordered Structures in Relaxors and Related Ferroelectrics

2.1 Lead-free relaxor perovskites based on BaTiO₃

Lead-free perovskite relaxors have recently attracted much attention as capacitive energy storage materials due to the higher recoverable energy density compared to traditional, ferroelectric-based (i.e., BaTiO₃-based) capacitors. The recoverable energy density in a parallel-plate capacitor is defined by the following equation:

$$J_{\rm rec} = \int_{P_{\rm r}}^{P_{\rm s}} E \, dP,\tag{1}$$

where P_s and P_r are the saturation and remanent polarizations measured upon capacitor charging and discharging, respectively, in a typical polarization–electric field hysteresis loop (*P*–*E* loop), as reported in Fig. 1.¹⁸⁾

In BaTiO₃-based ferroelectrics below the Curie temperature (T_c), a cooperative long-range cation displacement occurs at the *B*-site of the *ABO*₃ perovskite structure, which drives the appearance of mesoscopic polar domains throughout the lattice.¹⁹⁾ These so-called ferroelectric domains are the reason for the high dielectric permittivity of such materials. Upon electric field application during charging of the capacitor, above a certain threshold (coercive field, E_c) the domains switch in the direction of the applied electric field; J. Phys. Soc. Jpn. Downloaded from journals.jps.jp by 193.171.83.215 on 08/30/22

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Table I. Possible Me^x cation substitution schemes in BaTiO ₃ .					
Perovskite site	Substituted cation	Homovalent	Heterovalent (donor)	Heterovalent (acceptor)	Dipole- compensated
A	Ba ²⁺	Me ²⁺	Me^{3+} Charge compensation: $V_A{''}$ or $V_B{''''}$	Me ⁺ Charge compensation: V _O .	$Me^+ + Me^{3+}$
В	Ti ⁴⁺	Me ⁴⁺	Me^{5+} Charge compensation: $V_A{''}$ or $V_B{''''}$	Me ³⁺ Charge compensation: V _O .	$Me^{3+} + Me^{5+}$ $Me^{2+} + Me^{6+}$



Fig. 2. (Color online) Comparison between ferroelectric and relaxor perovskites. Ferroelectrics have low recoverable energy density (the green shaded area) compared to relaxors because of the presence of cooperative long-range cation displacement creating mesoscopic polar domains. Relaxor behavior can be induced by chemical substitution aimed at modifying both size and distribution of the polar domains, thereby disrupting long-range polar correlation.^{21,22}) This figure is taken from Ref. 21 © 2005 American Physical Society and Ref. 22 © 2009 American Physical Society.

the full charge of the capacitor is attained when no further domains can be switched by the applied electric field, or in other words when the saturation state, P_s , is reached. Upon capacitor discharging in ferroelectric materials, at E = 0 the remanent state is reached, where ferroelectric domains are still largely oriented in the previously applied field direction. This means that, if P_r is high, only a portion of the initially stored electric energy can be recovered during discharge (cf. Fig. 1).

Relaxor materials, on the other hand, possess a slim P-E loop (i.e., P_r is close to zero),²⁰⁾ which brings about a higher recoverable energy density compared to the ferroelectric case (cf. Fig. 2). The reason is the disruption of long-range correlation of *B*-site displacements through either *A*- or *B*-site ionic substitution in the perovskite lattice. The disorder associated with substituents contributes to reducing the remanent polarization by reducing the overall size of polar domains (i.e., the domains in which a polar correlation still exists). Consequently, relaxor compositions have a slim hysteresis loop, but at the expense of reducing the dielectric permittivity (hence reducing P_s compared to the ferroelectric



Fig. 3. (Color online) Dependence of T_c or T_m on substituent percentage for *A*-site homovalent (filled circles) and *B*-site homovalent (empty circles), *A*-site heterovalent (filled squares) and *B*-site heterovalent (empty squares) substituted BaTiO₃.^{25–33}) In brackets, the ionic radii in Å obtained from Shannon.³⁴) The crossover to relaxor compositions is marked as asterisks for every substituent. Adapted from Veerapandiyan et al.²⁴) This figure is taken from Ref. 24 © 2020 The Authors.

case). In order to achieve high recoverable energy density, a trade-off must then be found between $P_{\rm r}$ reduction and $P_{\rm s}$ stabilization, which is generally available in crossover compositions between ferroelectric and relaxor state.^{23,24)}

It is universally accepted that relaxor behavior can be induced in BaTiO₃ perovskites by chemical modification. Typical substitutions in BaTiO₃ involve either A- or Bcations, where Ba²⁺ or Ti⁴⁺ is substituted by either homovalent or heterovalent species, or in a dipole-compensated way (cf. Table I). Interestingly, different types of A- or B-site substitution can give very different results in terms of both the introduction of relaxor behavior and the temperature dependence of the dielectric permittivity. Figure 3 displays the T_c or the T_m (maximum of dielectric permittivity) for several BaTiO₃ solid solutions.²⁴⁾ Heterovalent substituted systems display a steeper decrease in T_c or T_m compared to homovalent substituted systems. A-site homovalent substituted systems (with Sr^{2+} and Ca^{2+} replacing Ba^{2+}) do not display relaxor behavior up to 45% substitution concentration, whereas heterovalent A-site substituents (like La^{3+} or Pr^{3+}) induce relaxor behavior already at ~5% concentration. In homovalent *B*-site substituted BaTiO₃ (with Hf⁴⁺, Zr^{4+} , or Ce^{4+}) a high amount of substituent is necessary to induce relaxor behavior (generally above 20%), whereas in the heterovalent case $(Nb^{5+}) \sim 5\%$ is sufficient. Considering that only heterovalent substitution involving the B-site (either with substituent or charge compensation) has a strong effect in inducing relaxor behavior, it can be envisaged that hyperordered lattice structures (HOSs)-in the form of donor/



Fig. 4. (a) Frequency-dependent relative dielectric permittivity in $Ba_{0.60}Sr_{0.40}TiO_3$ (BST40) and $Ba_{0.60}Sr_{0.20}Ca_{0.20}TiO_3$ (BSCT20) as a function of temperature. No frequency dispersion but only a diffuse phase transition is obtained.³⁵⁾ (b) Frequency-dependent relative dielectric permittivity for $0.20Na_{0.5}Bi_{0.5}TiO_3$ -0.80BaTiO₃ (NBT20-80) as a function of temperature. Also here only a diffuse phase transition without frequency dispersion is obtained. Frequency values: 1: 10² Hz, 2: 10³ Hz, 3: 10⁴ Hz, 4: 10⁵ Hz, 5: 2.5 × 10⁵ Hz, 6: 5 × 10⁵ Hz, 7: 10⁶ Hz.⁴⁰ (c) Parallel capacitance, C_P, and permittivity (ϵ') as a function of frequency and temperature for $Ba_{0.90}La_{0.10}TiO_3$. Frequency dispersion typical of a relaxor material is obtained.²⁶⁾ This figure is taken from (a) Ref. 35 © 2007 Elsevier, (b) Ref. 40 © 2008 Elsevier, (c) Ref. 26 © 1999 American Institute of Physics.

acceptor substituent cations and the related charge-compensating cation/anion vacancies—have a relevant role in this phenomenon.

2.2 A-site substituted $BaTiO_3$

The A-site of $BaTiO_3$ is occupied by Ba^{2+} , with an effective ionic radius $R_{\text{Ba}} = 1.61 \text{ Å}.^{34}$ Substituting it with a smaller homovalent cation increases the cubic lattice fraction thereby decreasing T_c and without inducing relaxor-like frequency dispersion at least below 45% substituent content. This is the case, for instance, of Sr^{2+} ($R_{\text{Sr}} = 1.44 \text{ Å}$) substitution, which is essentially a mixture of the BaTiO₃ ferroelectric with the SrTiO₃ incipient ferroelectric.^{35,36)} In this case, only a diffuse phase transition is attained, with permittivity maximum (i.e., T_m) shifted to around room temperature for a Sr^{2+} content between 20 and 40% [cf. Fig. 4(a)].³⁵⁾ Note here that a relaxor material presents frequency dispersion of the permittivity vs T curve, where the permittivity maximum (Tm) must obey the Vogel-Fulcher relation. On the other hand, if a material presents a diffuse phase transition, the permittivity maximum is broad over a large range of temperatures but not frequency dispersed. A different picture is obtained if the substituent cation has stereochemical activity, that is, it possesses an electron lone pair capable of forming a covalent bond with the oxygen atoms neighboring the A-site.^{37,38)} In this case, an increase in $T_{\rm c}$ and in overall lattice tetragonality is obtained, as it has been observed by either substituting Pb^{2+} ($R_{Pb} = 1.49 \text{ Å}$) or the combination of Bi^{3+} and Na^+ ($R_{Bi} = 1.45 \text{ Å}^{39}$) and $R_{\rm Na} = 1.39 \,\text{\AA}$ — in this case a dipole-compensated substitution) at the A-site of the perovskite-type structure [cf. Fig. 4(b)].⁴¹⁾ Another peculiar example is that of Ca^{2+} substituting at the A-site. Although Ca^{2+} is considerably smaller than the host Ba^{2+} cation ($R_{Ca} = 1.34 \text{ Å}$), increasing the amount of Ca^{2+} at the A-site at first produces an increase of the Curie temperature, followed by a slight decrease for higher substituent contents.⁴²⁾ This behavior has been ascribed to a competition between the strain induced by the substantial size mismatch between Ba2+ and Ca2+ and absolute (tolerance factor-related) size effects. Interestingly, also in the case of Ca²⁺ an increased lattice polarization component was observed, although stereochemical arguments cannot be invoked here. Levin et al.⁴³⁾ and Fu et al.⁴²⁾ were able to explain this with a quantum ferroelectric transition producing *A*- and *B*-site cooperative displacements in Ca-substituted BaTiO₃, which is induced by Ca off-centering mitigating the strain mismatch induced by size variance.^{42,43}

Based on these arguments, one could conclude that A-site substitution of BaTiO₃ mainly influences the lattice parameters, promoting either cubic or tetragonal distortion depending on the introduced species, thereby acting as a shifter or a stabilizer for the T_c , which in turn decreases or increases lattice permittivity, respectively. Diffuse phase transitions may be induced, but without typical relaxor-like frequency dispersion in the relative permittivity response. These considerations indeed apply to A-site homovalent or dipolecompensated substitution types, but cannot be applied to heterovalent A-site substitution, where on the other hand the onset of relaxor behavior has been observed. This is exemplified by the case of La-substituted BaTiO₃. La³⁺ has an ionic radius of 1.36 Å and substitutes at the perovskite Asite.³⁴⁾ Structural studies of this system evidenced transition from tetragonal to pseudocubic lattice already at 5% La^{3+} content. This is associated with the disappearance of polar phonon modes generally related to ferroelectric long-range order.²⁶⁾ Above 7% La³⁺ content a broad, frequencydispersed dielectric permittivity vs T curve was measured, which underlines transition to relaxor state [cf. Fig. 4(c)]. The permittivity peak (T_m) shifts down to well below room temperature in compositions with >7% La³⁺ content. Further Raman studies evidenced the presence of a sharp extra-mode at $\sim 830 \,\mathrm{cm}^{-1}$, which was tentatively ascribed to the presence of Ti vacancies as charge compensation scheme.⁴⁴⁾ In fact, being La^{3+} a donor A-site substituent, it is conceivable that either Ba or Ti vacancies are present in the lattice as a charge compensation mechanism. As explained in the next section, the assumption by Pokorny et al. about Ti vacancies is correct for La³⁺ substitution, and is also the reason for appearance of relaxor behavior: it is the disruption of longrange correlation of Ti displacements that produces relaxor behavior and thus the B-site must be involved for relaxor behavior to appear.^{28,45)} This occurs in A-site donor substituted systems with charge compensation via B-site cation vacancies. The combination of A-site donor substituents with B-site cation vacancies can be considered as a HOS

affecting the local displacements of Ti cations and acting as a disruptor of ferroelectric long-range order, reducing both the mobility and the size of ferroelectric domains, thereby inducing relaxor behavior.

2.3 B-site substituted BaTiO₃

The *B*-site of BaTiO₃ is occupied by Ti^{4+} , with an effective ionic radius $R_{\text{Ti}} = 0.61 \text{ Å}.^{34}$ Homovalent *B*-site substitution involves generally a larger cation like Sn^{4+} ($R_{\text{Sn}} = 0.69 \text{ Å}$), Zr^{4+} ($R_{\text{Zr}} = 0.72 \text{ Å}$) or Ce^{4+} ($R_{\text{Ce}} = 0.87 \text{ Å}$) as substituents. The effect of this substitution, in terms of dielectric properties, is a shift of T_c or T_m to lower temperatures, the onset of a diffuse phase transition, and relaxor behavior appearing generally above ~20% substituent content. The structural transition has been evidenced in many homovalent systems and is always alike: by increasing the substituent content the polymorphic phase boundaries of BaTiO₃ merge into a so-called "tricritical" point at ~10% substituent content, over which direct (albeit diffuse) transition from rhombohedral ferroelectric to cubic paraelectric phase is attained.^{28,29,46-50)} Above ~15-20% substituent content the ferroelectric-paraelectric transition lies below room temperature, whereas above $\sim 20\%$ — depending in general from ionic size^{24,28}) — relaxor behavior is reached [cf. Fig. 5(a) for Zr⁴⁺-substituted BaTiO₃]. The evolution of the dielectric properties and of the structural phase transitions in B-site homovalent-substituted BaTiO₃ can be interpreted as follows: since large B-site cations promote a non-polar perovskite lattice (BaZrO₃, for instance, is paraelectric⁵¹), introducing such cations into BaTiO₃ is tantamount to creating local nonpolar regions within a ferroelectric matrix. This produces at first a merging of the phase boundaries into the tricritical point, and then a diffuse phase transition. Above a certain substituent amount, the ferroelectric matrix starts being disrupted on the long range, and relaxor behavior appears. The polar nanoregions or nanoclusters underpinning relaxor behavior are thus confined to the Ti-containing unit cells and their ensembles.^{52,53)}

Heterovalent B-site substitution produces a very similar evolution of both the structure and the dielectric properties of BaTiO₃ materials, albeit drastically shifted towards lower substituent content: Taking as example Nb-substituted BaTiO₃, merging of phase transitions (similar to the tricritical point of homovalent substituted systems) is attained already between $\sim 5-7\%$ substituent content, and relaxor behavior appears for >10% Nb⁵⁺ added^{25,54)}—cf. Fig. 5(b). Recent Nuclear Magnetic Resonance (NMR) studies evidenced that Nb⁵⁺ is more effective in inducing lattice disorder in the BaTiO₃ lattice, compared to homovalent substituents. Veerapandiyan et al. compared ¹³⁷Ba NMR results in the $BaZr_{x}Ti_{1-x}O_{3}$ and $BaNb_{x}Ti_{1-x}O_{3}$ systems [cf. Fig. 6(a)], and evidenced that the mean quadrupolar coupling constant (C_0) , a parameter that reflects the extent of local structural disorder for the Ba²⁺ site,⁵⁵⁾ has similar values in BaZr_{0.30}Ti_{0.70}O₃ and $BaNb_{0.07}Ti_{0.93}O_3$, which means that just 7% of Nb⁵⁺ is able to create in BaTiO₃ a similar amount of disorder as 30% Zr⁴⁺.⁵⁴⁾ In that work, the NMR results were corroborated by composition-dependent Raman spectroscopy on both systems, which showed [as reported in Fig. 6(b)] that the ferroelectric order, which is present at room temperature (RT) up to >10% Zr^{4+} content, is already lost at RT with 7% Nb⁵⁺



Fig. 5. (Color online) (a) Relative dielectric permittivity as a function of composition, frequency and temperature for (a) $BaZr_xTi_{1-x}O_3$ (BZT100*x*) and (b) $BaNb_xTi_{1-x}O_3$ (BNbT100*x*). The permittivity curve for $BaTiO_3$ (BTO) is also reported for comparison. Relaxor behavior is evident in BZT at x = 0.40, and at x = 0.07 in BNbT. This figure is taken from Ref. 54 © 2022 The Authors.



Fig. 6. (Color online) (a) Mean quadropolar coupling constant (CQ) fitted with Czjzek model referred to 137Ba NMR data for $BaZr_xTi_{1-x}O_3$ (BZT) and $BaNb_xTi_{1-x}O_3$ (BNbT), measured at 117 and 133 °C, respectively, to avoid the influence of symmetry breaking in a polar lattice structure. (b) Composition-dependent Raman spectra for BZT and BNbT. The Raman spectrum of pure $BaTiO_3$ (BTO) is reported for comparison.⁵⁴) This figure is taken from Ref. 54 © 2022 The Authors.

added. The absence of ferroelectric order is symbolized in the Raman spectra reported in Fig. 6(b) by the disappearance of the peak at ~300 cm⁻¹, which is related to long-range ferroelectricity.^{56,57)} Interestingly, the Raman spectra of the Nb⁵⁺-substituted material reveal the presence—at ~830 cm⁻¹—of a sharp extra-mode similar to the one recorded in La³⁺-substituted BaTiO₃ and ascribed by Pokorny et al. to



Fig. 7. (Color online) Raman spectra of pure BaTiO₃ (BT), Nb⁵⁺-substituted BaTiO₃ (BNbT), La³⁺-substituted BaTiO₃ (BLaT), and BaTiO₃ co-substituted with Ga³⁺ and Nb⁵⁺ (BGaNbT). The mode at ~830 cm⁻¹ (mode 7) is present only in the BNbT and BLaT systems.⁵⁸⁾ This figure is taken from Ref. 58 © 2022 The Authors.

the presence of B-site vacancies as charge-compensating defects.44) Recent work allowed to unambiguously assign this mode as a localized oxygen breathing vibration around B-site vacancies. First and foremost, this mode does not appear in BaTiO₃ solid solutions where charge (ionic) compensation involving the B-site cannot occur, such as in homovalent or dipole-compensated substituted systems. This can be easily seen in Fig. 7, where Veerapandiyan et al. compared Raman spectra of Nb5+- and La3+-substituted BaTiO3 (BNbT and BLaT, respectively) with pure BaTiO₃ (BT) and a dipolecompensated solid solution where Ti⁴⁺ is partly replaced by Ga³⁺ and Nb⁵⁺ in equal amount (BGaNbT). Only in the systems requiring charge compensation (BNbT and BLaT) is the mode at $\sim 830 \text{ cm}^{-1}$ (here displayed as "mode 7") present. We caution the reader that in the systems treated here always ionic charge compensation is meant; electronic compensation can also occur, but is restricted to low substituent contents.⁵⁸⁾

Veerapandiyan et al. recently carried out further studies to improve this understanding by using Density Functional Theory (DFT) to simulate Raman spectra belonging to different atomic arrangements.⁵⁴⁾ They constructed $3 \times 3 \times 3$ BaTiO₃ supercells (i.e., with 27 Ti sites) and calculated Raman spectra using the spherical averaging method which allows to calculate realistic Raman spectral signatures in polycrystalline materials⁵⁹⁾—according to the following substitution schemes:

- One Ti⁴⁺ atom replaced by one Zr⁴⁺.
- Four Ti⁴⁺ atoms replaced by Nb⁵⁺ cations, one Ti⁴⁺ replaced by a Ti (*B*-site) vacancy (V_{Ti}^{''''}).
- Two Ti²⁺ atoms replaced by Nb⁵⁺ cations, one Ba²⁺ replaced by a Ba (A-site) vacancy (V_{Ba}'').

The results of this analysis can be seen in Fig. 8. The sharp mode at ~830 cm⁻¹ is absent in homovalent-substituted BaZr_{0.40}Ti_{0.60}O₃ (BZT40). In heterovalent-substituted BaNb_{0.15}Ti_{0.85}O₃ (BNbT15), on the other hand, it is present only when Ti vacancies are considered as the charge compensation scheme.⁴⁴⁾ This result confirms unambiguously that in donor-substituted BaTiO₃ (both at *A*- and *B*-site), Ti vacancies are the preferred charge compensation scheme. This evidences — also in the case of *B*-site substituted



Fig. 8. (Color online) Experimental and calculated (grey line) Raman spectra of (a) $BaZr_{0.40}Ti_{0.60}O_3$ (BZT40) and (b) $BaNb_{0.15}Ti_{0.85}O_3$ (BNbT15). The sharp mode at ~830 cm⁻¹ is absent in homovalent-substituted BZT40, and in heterovalent-substituted BNbT15 is present only when Ti vacancies are considered as the charge compensation scheme.⁵⁴ This figure is taken from Ref. 54 © 2022 The Authors.



Fig. 9. (Color online) Hyper-ordered structure in Nb⁵⁺-substituted BaTiO₃, constituted by four Nb⁵⁺ cations and one $V_{Ti}^{\prime\prime\prime\prime}$. Both planar (a) and bent (b) configurations can be found. The diagrams display only the perovskite B-site and do not show the Ba and O atoms of the perovskite structure. The crossed ball in the center symbolizes the Ti vacancy.⁵⁴⁾ This figure is taken from Ref. 54 © 2022 The Authors.

 $BaTiO_3$ —the presence of HOSs. These are constituted in this case by *B*-site donor substituent—*B*-site vacancy pairs. These electrically charged defect arrangements could—similar to the *A*-site donor substitution case—affect the local displacements of Ti cations and disrupt the long-range ferroelectric order, inducing lattice disorder and, ultimately, relaxor behavior.

2.4 Role of hyper-ordered structures in relaxor behavior of BaTiO₃ solid solutions

As explained previously, in heterovalent-substituted Ba-TiO₃, HOSs consisting of donor substituents (*A*- or *B*-site) and *B*-site charge compensating defects (*B*-site vacancies) are present. These structures have a strongly localized character, since energy considerations require donor substituents to occupy sites in unit cells next to *B*-site vacancies.⁵⁴⁾ In the case of Nb⁵⁺-substituted BaTiO₃, these structures are constituted by Ti vacancies and surrounding Nb⁵⁺ cations, which can assume either a planar or a bent configuration [cf. Figs. 9(a) and 9(b)⁵⁴⁾]. The role of HOSs in inducing relaxor behavior was investigated recently by Veerapandiyan et al. using DFT calculations to clarify the effect of Zr⁴⁺ or Nb⁵⁺ addition (in the latter case with charge compensation by Ti vacancies) on the volume and total electric potential of the



Fig. 10. (Color online) Local 5-atom unit cell volume and total electric potential change in BZT (a, c) and BNbT (b, d), respectively, as obtained from DFT calculations. Local volume change of each unit cell and the corresponding absolute change of total electric potential with respect to pure BaTiO₃ is presented, showing the strong impact on the local structure of Nb⁵⁺ substitution and the related hyper-ordered structure, extending to several unit cells compared to the weak and very localized influence of Zt^{4+} substitution.⁵⁴ This figure is taken from Ref. 54 © 2022 The Authors.

BaTiO₃ lattice, as shown in Fig. 10. In the calculations, $5 \times 5 \times 5$ supercells were considered, in which four Ti⁴⁺ atoms are replaced by four Zr⁴⁺ atoms and five Ti⁴⁺ atoms are replaced by four Nb⁵⁺ atoms and one Ti vacancy, for BZT and BNbT, respectively (i.e., amounting to 3.2% substitution concentration for both BZT and BNbT). In the case of BZT, a so-called "special-quasirandom structure" was constructed, which is the supercell of a given size, where dopants are distributed in such a way that the short-range order parameters are as close as possible to the ones of a completely random (infinite) structure. In the case of BNbT, in contrast, the Nb atoms were arranged as a hyper-ordered structure in form of a cluster around the Ti-vacancy as required by the minimization of the electrostatic energy.⁵⁴⁾ To analyze the local strain caused by substituents, the local volume was calculated using the eight nearest neighboring Ba^{2+} ions surrounding the *B*-site ions of each unit cell within the supercell. A comparison of these values to pure rhombohedral BaTiO₃ yields a relative change in local volume [cf. Figs. 10(a) and 10(b) for BZT and BNbT, respectively]. The change in total electric potential in BZT [Fig. 10(c)] and BNbT [Fig. 10(d)] was estimated for planes spanned by *B*-site ions by computing the difference to the pure BaTiO₃ system. As can clearly be seen, in BZT, there is a large strain difference in the vicinity of Zr atoms, impacting beyond the nearest-neighbor B-site, but the potential difference is confined to the Zr atom. In BNbT, on the other hand, the effect of the HOS is very strong both in terms of strain and electrical potential, and its effect is "felt" over a wide range of the supercell. This result again confirms the initial supposition that only in BNbT a charge-related mechanism is at the basis of the disruption of ferroelectric long-range order, and that the localized random fields induced by the presence of the HOSs can influence the direction of Ti⁴⁺ and Nb⁵⁺ cation displacements in several neighboring unit cells, inducing the strong lattice disorder detected by NMR and Raman, and the "early" relaxor behavior in BNbT systems. On the other hand, in BZT only strain effects result from the difference in B-site ionic radii and the extent of this effect is drastically smaller than the strain difference observed in BNbT due to the presence of HOSs. Hence, much higher substituent content is necessary in homovalent relaxors to effectively disrupt long-range ferroelectric order, and thus to induce relaxor behavior.⁵⁴⁾ These results underline the prominent role of charged HOSs in the definition of dielectric properties in BaTiO₃-based solid solutions. Their role is evident also in *B*-site dipole-compensated systems like BaGa_xTa_xTi_{1-2x}O₃, where the introduction of the same amount of Ga³⁺ and Ta⁵⁺ does not require any vacancy to appear for charge compensation:⁶⁰⁾ in such system relaxor behavior also appears for very low substituent contents ($x = \sim 0.05$). It can thus be envisaged that, in absence of cation vacancies, the introduction of differently charged cations may induce HOSs that can heavily influence the long-range ferroelectric order.

3. Hyper-Ordered Structures for Permittivity Boosting of Paraelectric Materials

3.1 Electron-pinned defect dipoles

An emerging concept to design colossal permittivity materials has recently been proposed by Hu et al.¹⁷⁾ In their report, the modified rutile-type TiO₂, Ti⁴⁺ of which is partially substituted by nominally equal amounts of Nb⁵⁺ and In^{3+} , shows extremely large relative permittivity of the order of 10⁴ over a wide temperature range across room temperature. The observed permittivity is greater by two orders of magnitude than the initial value of rutile-type TiO₂, suggesting an innovative way to boost the permittivity of dielectric materials. An origin of the colossal permittivity was attributed to special defect complexes, which are named as "electron-pinned defect dipoles (EPDD)", invoking HOSs embedded in the host matrix. The concept of EPDD suggests that the co-doping of Nb⁵⁺ and In³⁺ induces "triangle" shaped $In^{3+}_{2}Vo^{\bullet\bullet}Ti^{3+}$ and "diamond" shaped $Nb^{5+}_{2}Ti^{3+}A_{Ti}$ $(A = Ti^{3+}/In^{3+}/Ti^{4+})$ in the matrix, and their close correlation gives rise to defect dipole clusters, around which electrons are localized to cause large polarizability.¹⁷⁾ Inspired by this report, extensive researches have been performed to develop EPDD-based dielectric materials with colossal permittivity.^{61–66)} Several follow-up studies, however, pointed out the contribution of apparent polarization response due to accumulated carriers in the grain boundaries to the colossal J. Phys. Soc. Jpn. 91, 091001 (2022)

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Fig. 11. (Color online) (a) Dielectric permittivity of the $(Nb_{0.5}In_{0.5})_{0.005}$ -Ti_{0.995}O₂ (NITO-0.5) single crystal measured along the crystallographic [001] direction, which is plotted as a function of temperature and frequency. (b) The Arrhenius plot for the dielectric relaxation observed in NITO-0.5.

permittivity like the case of CaCu₃Ti₄O₁₂ (CCTO).^{10–12,67,68)} Micro-contact *I–V* measurements on the polycrystalline (Nb+In) co-doped TiO₂, for instance, have clarified the coexistence of semiconducting grains and highly insulating grain boundaries to form microscopic barrier layer capacitors.⁶⁹⁾ In the amorphous TiO₂ film, on the other hand, the permittivity enhancement was also obtained by the Nb+In co-doping even though the system is free from grain boundaries.⁷⁰⁾ Because of these apparently incompatible results, the origin of colossal permittivity in (Nb+In) co-doped TiO₂ still remains controversial.

3.2 Dielectric response in the (Nb+In) co-doped TiO₂ single crystals

Figure 11(a) presents the dielectric permittivity measured in the single crystal of $(Nb_{0.5}In_{0.5})_xTi_{1-x}O_2$ with x = 0.5%(NITO-0.5) along the crystallographic [001] direction, which is plotted as a function of temperature and frequency. As shown in the figure, huge permittivity of the order of 10^4 is observed at 30 K even for the single crystal without grain boundaries. Since the color of the NITO-0.5 single crystals, which are synthesized with a floating-zone (FZ) method, are black alike the polycrystalline samples, it is expected that they have semiconducting characteristic as observed in the inside of individual grains in the polycrystalline samples. When the dielectric measurements are performed in such semiconducting samples, the Schottky barrier often forms at the sample-electrode interfaces to give rise to apparently large dielectric response due to the barrier layer capacitor effect. Figure 12 shows the frequency dispersion of real (ε') and imaginary (ε'') parts of complex permittivity for (a) NITO-0.5 and (b) NITO-2.0 measured at various test electric fields from 1 to 10 V/cm. Both for NITO-0.5 and NITO-2.0,



Fig. 12. (Color online) The frequency dispersion of real part (top panel) and imaginary part (bottom panel) of complex permittivity for (a) NITO-0.5 and (b) NITO-2.0 single crystals, which were measured with several electric fields from 1 to 10 V/cm. Insets of the panels presents the electric-field-dependence of real and imaginary parts of the complex permittivity measured at 100 Hz.

strong electric-field-dependence is found in the real (ε') and imaginary (ε'') parts of permittivity in the low-frequency region below 10^3 Hz. As presented in the insets of Figs. 12(a) and 12(b), furthermore, it has been clarified that ε' and ε'' show mutually opposite trend in the low-frequency region with increment of the applied electric field; ε' decreases with elevating the electric field whereas ε'' increases. This result agrees with that expected in the barrier layer capacitor effect, suggesting that the huge permittivity of the order of 10^4 observed in the (Nb+In) co-doped TiO₂ is not the intrinsic dielectric permittivity of the material. Judging with the results of follow-up studies,^{67–69)} the barrier layer capacitor effect, which is caused by combination of the semiconducting bulk and the insulating grain boundaries and/or the Schottky barriers at the sample-electrode interfaces, plays a major role in the dielectric response of Nb+In co-doped TiO₂ in the high-temperature region.



Fig. 13. (a) Temperature dependence of permittivity for NITO-0.5 along the [001] direction measured with a test frequency of 1 MHz (open circles), where the inset indicates the magnified view of the low-temperature region below 13 K. Note that open squares and crosses in the inset denote the permittivity of the pristine TiO_2 , which was observed by the author's group and extracted from Ref. 71, respectively. (b) Frequency dispersion of permittivity for NITO-0.5 along [001] and [110] directions observed at 2 K. The corresponding values of permittivity in the pristine TiO_2 are indicated by the broken lines in the panel for comparison.

In the low-temperature region, on the other hand, the permittivity steeply drops successively from the higher frequency as presented in Fig. 11(a). This result indicates disappearance of the barrier layer capacitor effect in the sufficiently low-temperature region, where the thermally excited mobile carriers are expected to be frozen to render the NITO-0.5 highly insulating. Note that analyses of the observed dielectric relaxation with Arrhenius plot gives an activation energy of 7.6 meV for the carrier excitation [Fig. 11(b)]. Figure 13(a) shows the temperature dependence of permittivity for NITO-0.5 measured along the [001] direction with the test frequency of 1 MHz (open circles). The inset of the Fig. 13(a) presents the magnified view for the temperature range below 13 K, where the apparently huge permittivity disappears due to the quench of thermally excited carriers. Open squares and crosses in the inset denote the permittivity (// [001]) of the pristine TiO₂, measured by the author's group and extracted from Ref. 71, respectively. In the lowest temperature of around 2 K, as shown in the inset, NITO-0.5 has been found to show the permittivity of approximately 1,000, which is much greater than the pristine TiO₂'s even though the barrier layer capacitor effect disappears. This discovery has demonstrated the intrinsic effect of the Nb+In co-doping to induce HOSs, by which the permittivity of TiO₂ certainly increases though the magnitude is not so huge as initially reported in Ref. 17. Figure 13(b) shows the frequency dispersion of permittivity for NITO-0.5 measured at 2 K along the [001] and the [110] directions, where each permittivity of the pristine TiO₂ is indicated by the broken line for comparison. As shown in the figure, the permittivity along the [001] direction increases intrinsically by approximately 700 with the Nb+In co-doping. This result verifies the potential of EPDD for the permittivity bosting as a functional HOSs. Along the [110] direction, on the other hand, the permittivity is also enhanced by the co-doping though its magnitude is a little bit smaller than that along the [001] direction.

3.3 Post annealing effect on the (Nb+In) co-doped TiO₂ single crystals

As the average valence of co-dopants is selected to be



Fig. 14. Frequency dispersion of permittivity and $\tan \delta$ for NITO-2.0 along (a) the [001] and (b) the [110] directions observed at 2 K. The corresponding values of permittivity in the pristine TiO₂ are indicated by the arrows in the panels for comparison.

nominally same as Ti^{4+} , the semiconducting nature of the (Nb+In) co-doped TiO₂ single crystals evokes existence of oxygen vacancies and/or partial non-stoichiometry of co-dopants to generate Ti^{3+} in the matrix. Inspired by a conventional knowledge that the post annealing with an appropriate condition often cures the oxygen vacancy and inhomogeneity in materials, an influence of the post annealing on the semiconducting (Nb+In) co-doped TiO_2 single crystals has been examined under the condition where the co-doped samples were covered by TiO_2 powder during the post-annealing.

Figures 14(a) and 14(b) present the frequency dispersion of permittivity and tan δ for as-grown NITO-2.0 measured at 4 K along the crystallographic directions of [001] and [110], respectively. The arrows in the panels denote the permittivity of the pristine TiO₂ single crystal of rutile-type at 1.6 K along the [001] and the [110] directions.⁷¹⁾ As seen in the figure, the permittivity and tan δ of NITO-2.0 show monotonous frequency dependence both along the [001] and the [110] directions, indicating no dielectric relaxation occurs until 10⁶ Hz. This result confirms that the extrinsic dielectric responses due to the barrier layer capacitor effect are completely suppressed at this temperature, since they usually



Fig. 15. (a) The post-annealing effect on the permittivity of NITO-2.0 at 100 kHz along the [001] direction. (b) Permittivity of the as-grown (solid circles) and the post-annealed (open circles) samples plotted as a function of the co-dopant concentration *x*, where the samples were subjected to the post-annealing at 1273 K for 100 h in TiO₂ powder. (c) The magnified view for the data of the post-annealed samples. Note that the arrows in the panels (a) and (b) indicate the corresponding value of the pristine TiO₂ single crystal for comparison.

give rise to the dielectric relaxation in the low frequency region. The permittivity of NITO-2.0 is found to be larger by several times than that of the pristine TiO₂ both for the [001] and the [110] directions over the entire frequency range observed here as in the case of NITO-0.5. Note that a gradual drop of tan δ around 10⁶ Hz in the panel (b) is an artifact.

Figure 15(a) depicts a variation of the permittivity with the post-annealing for NITO-2.0, where the data were measured along the [001] direction with the test frequency of 100 kHz at 4 K. In the as-grown sample, the initial permittivity of NITO-2.0 is approximately 1,300 as shown in the figure. As the sample is subjected to the post-annealing in TiO₂ powder for 10h at 1000 °C, the permittivity of NITO-2.0 steeply decreases to 630. On further increment of the annealing time, it keeps gradual decrease and almost saturates at the annealing time of 50h with a value of about 390, which is approximately sesquialteral of the pristine TiO₂'s. This result suggests that the post-annealing induces rearrangement of the defect complex into the one having less polarizability than that in the as-grown co-doped single crystal. It should be noted here that the color of the single crystal was found to stay black and the apparent huge permittivity in the high temperature region still survives even after the postannealing.

The effect of post-annealing on the dielectric response of NITO-x is presented in Fig. 15(b) as a function of the codopant concentration x, where solid and open circles respectively indicate the permittivity for the as-grown and the post-annealed samples, which were measured with the test frequency of 100 kHz at 4 K. Note that the post-annealed samples were baked at 1273 K for 100 h in TiO₂ powder. Figure 15(c), on the other hand, presents the magnified view for the results of post-annealed samples. As shown in the figure, the permittivity of the as-grown NITO-x along the [001] direction monotonically increases as x increases, suggesting the number of EPDD directly relates with the co-dopant concentration. In contrast to the as-grown samples, the value of permittivity in the post annealed samples gradually decreases with x, from approximately 450 at x =0.2% to approximately 390 at x = 2% as shown in Fig. 15(c). If the co-dopants create the EPDD among themselves apiece also in the post-annealed samples, it is expected that the permittivity monotonically increases with x in the qualitatively same trend as observed in the as-grown samples. Therefore, the mutually opposite trend between the as-grown and the post-annealed samples implies that the post-annealing induces relatively extensive reconfigurations of defect structures. It is also possible that the stoichiometry of dopants slightly changes due to the post-annealing through a diffusion-driven exchange of elements between the sample and the surrounding TiO₂ powders. This nontrivial postannealing effects indicates that a wide spectrum of HOSs can form through the arrangement of co-dopants and the fabrication process, and thereby various dielectric responses are able to be obtained by design. A next step would be an elucidation of the composition-structure-property relationship of HOSs in the co-doped TiO₂. The comprehensive analyses of structures and chemical compositions in HOSs would pave a way to the development of functional dielectric materials of the next generation.

4. Conclusion

As discussed in the present review, a huge variety of HOSs form in ferroelectric and dielectric materials to give rise to useful functionalities, which can never be obtained in the homogeneous bulk or with local imperfections alone. The mutual interactions between the local imperfections and their surroundings induce HOSs to play a vital role in the macroscopic responses of the materials like polar nanoclusters in relaxors and EPDD in the co-doped TiO₂. Appropriate choices of substitution elements and controlling of their crystallographic locations enable flexible tuning of the phase transition properties of ferroelectric materials through controlled disruption of ferroelectric long-range order. The special combination of co-dopants has been found to induce unique defect complexes in the host matrix to enhance markedly the dielectric permittivity of the host materials. Although the elucidation of structure-property relationship in HOSs is still on a journey, it can update current materials science and provides a new concept for designing innovative electronic devices.

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