JCS-Japan

June
vol.129

Journal of the Ceramic Society of Japan

2021

SPECIAL ARTICLE

The 73th CerSJ Awards for Academic Achievements in Ceramic Science and Technology: Review

Defect chemistry in perovskite ferroelectrics—History, present status, and future prospects—

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Perovskite ferroelectrics such as BaTiO₃ and PbTiO₃ provide various functions arising from spontaneous polarization. Here, the history, present status, and future prospects of the defect chemistry for BaTiO₃ are described. Even for non-doped samples, unintentional impurities including Fe govern the defect chemistry and its related properties. By solving multiple nonlinear equations employing the thermodynamic data set reported, majority/minority defect-concentration diagrams are available not only in a high-temperature equilibrium state but also in a low-temperature quenched one. As an example, the defect diagrams of Ba(Ti,Ca)O₃ and Ba(Ti,Mn)O₃ are shown, and the roles of fixed valence (Ca) and variable-valence (Mn) acceptors are explained. I also introduce an example of the defect control in BaTiO₃ single crystals; an activation of visible-light photovoltaic effect, where two redox potentials derived from Fe²⁺ and Fe³⁺ act as scaffolds for generating electron-hole pairs.

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Key-words : BaTiO₃, PbTiO₃, Perovskite, Ferroelectric, Defect, Acceptor, Donor, Photovoltaic, Photocatalyst

[Received March 3, 2021; Accepted March 31, 2021]

1. Introduction

Perovskite oxides such as BaTiO₃ and PbTiO₃ are characterized by their polar structures with spatial inversion symmetry breaking.^{1)–3)} Spontaneous polarization (P_s) arising from off-center displacements of constituent atoms offers various functions such as high dielectric permittivity,⁴⁾ piezoelectricity,^{5),6)} ferroelectricity,^{7)–9)} electro-optics,^{9),10)} and photovoltaics (PVs).^{11)–13)} The high permittivity along with a moderate Curie temperature (T_C) of BaTiO₃ offers the unrivaled practical applications of multilayer ceramic capacitors (MLCCs).⁴⁾ At present, hundreds of MLCCs are utilized for a smart phone, and thousands of them are exploited for an automobile. For piezoelectric devices such as sensors, actuators, and transducers, Pb(Zr,Ti)O₃ is widely used,^{5),6)} while (Bi,Na)TiO₃ is employed for high-power piezoelectric applications.^{14),15)}

It is no exaggeration to say that the history and development of ferroelectrics and their related devices have been supported by defect control.^{4),16),17)} Even though the defect chemistry for SrTiO₃ and BaTiO₃ was established until early 1980 s^{18)–23)} and the role of transition metal dopants has been clearly understood,^{24)–26)} **Figure 1** shows the schematic defect structures of BaTiO₃, where the cubic symmetry is adopted for simplicity. The lattice is com-

Fig. 1. Schematics of (a) the perfect and (b) an actual crystal of BaTiO₃ (cubic). In reality, unintentional impurities such as Fe exist and govern the overall behavior of the defect chemistry. The acceptor impurity such as Fe³⁺ is accompanied by oxygen vacancy ($V_O^{\bullet\bullet}$) due to the charge neutrality.

posed of Ba²⁺ on the A site and O²⁻ on the face center, which is regarded as a close-packed structure; Ti⁴⁺ is positioned on the vicinity of the body center, the B site, surrounded by six of O²⁻. Because of configurational entropy, the perfect crystal displayed in Fig. 1(a) is never obtained, and the vacancies of Ba and Ti exist more or less. It is recognized that the concentrations of these cation vacancies are orders of magnitude lower than those of unintentional impurities.^{22),27),28)} Namely, the impurities such as Fe, as displayed in Fig. 1(b), govern the overall behavior of the defect chemistry and its related properties. In an oxidized sample, iron has a valence state of Fe³⁺ on the

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Ti⁴⁺ site, and the charge imbalance is compensated by a formation of oxygen vacancy ($V_{\text{O}}^{\bullet\bullet}$).^{26),29)} Cations on the interstitial sites are possible species, but these interstitial defects are negligible in perovskite oxides.²²⁾ All the concentrations of majority/minority defects can be obtained not only in a high-temperature (HT) equilibrium state but also in a low-temperature (LT) quenched state.^{24)–26)}

Moreover, an interaction between impurity ions and $V_{\text{O}}^{\bullet\bullet}$ is being understood.²⁹⁾ At present, intensive efforts have been devoted to the exploration of nanostructured materials and devices employing BaTiO₃ and related perovskites based on the defect chemistry,^{30)–47)} while the quantitative evaluation of defect concentrations along with defect control is far from complete even for traditional ferroelectrics such as Pb(Zr,Ti)O₃,^{48)–63)} (Bi,Na)TiO₃,^{64)–79)} (K,Na)NbO₃,^{80)–99)} and layered ferroelectrics such as Bi₄Ti₃O₁₂ including its related materials.^{100)–105)} This is because volatile elements of Pb, Bi and K are more or less released from samples during heating. If the concentration of A-site vacancies were strictly evaluated, the strategy for controlling defects and for establishing materials design can be provided. It seems that there is no means of accessing the absolute concentration of the A-site vacancies. For Bi-based ferroelectrics such as Bi₄Ti₃O₁₂^{104),106)–108)} and (Bi,Na)TiO₃^{66)–69)} etc., a high-oxygen pressure synthesis or crystal growth is effective for reducing the Bi vacancies from several percent to the order of thousand ppm (speculated indirectly) and the resultant samples exhibit superior ferroelectric and piezoelectric properties.

In this review, I describe the history, present status, and future prospects of the defect chemistry for BaTiO₃ as an example. First, I briefly mention the point-defect species, the history and the present status. Next, I address the role of fixed-valence (Ca) and variable-valence (Mn) acceptors on the defect concentration evolutions in a HT equilibrium state and in a LT quenched one (room temperature) along with the influence of equilibrium temperature. These result can be obtained by solving multiple nonlinear equations employing the thermodynamic data set of defect-related reactions reported in the pioneering studies.^{18)–26)} Third, I show an example of the defect control; an activation of visible-light PV effect in BaTiO₃ single crystals, where two redox potentials derived from Fe²⁺ and Fe³⁺ play an essential role. Lastly, I give an opinion on the future prospects of the defect chemistry involving rare-earth (RE) elements that is a major challenge to be overcome and the usefulness of two redox potentials for photocatalysts such as TiO₂ and SrTiO₃.

2. Defect chemistry

2.1 Kröger-Vink notation

From the past to the present, the nomenclature proposed by Kröger and Vinc, so called, the Kröger-Vink notation¹⁰⁹⁾ has been utilized to explicitly express defect species in crystalline solids. Here, I briefly explain its essence for BaTiO₃ as an example. **Figure 2** displays the format along with the usage. First, ‘I. What’ denotes an element (e.g., Ba, Ti, or O) or vacancy (*V*, where the italic is used to

Fig. 2. Kröger-Vink notation¹⁰⁹⁾ for explicitly expressing defect species in crystalline solids.

distinguish from vanadium). Second, ‘II. Where’ indicates the regular site in the host lattice, the Ba, the Ti, the O, or an interstitial site. Third, ‘III Charge’ shows the effective charge compared with the formal ionic charge of Ba²⁺, Ti⁴⁺, and O²⁻; ×: neutral, ′: one (singly) negative charge [′′: two (doubly) negative charges], and •: one (singly) positive charge [••: two (doubly) positive charges]. In a similar manner, electronic defects are denoted as *e*′ for electron and *h*• for hole.

2.2 Oxygen vacancy

One of the most important defects in metal oxides is oxygen vacancy, i.e., the vacancy on the O site. Compared with the formal ion of O²⁻, oxygen vacancy can have the following possible charged states: $V_{\text{O}}^{\bullet\bullet}$ with doubly positive charges, $V_{\text{O}}^{\bullet}$ with singly positive charge, and $V_{\text{O}}^{\times}$ with charge neutral. At extremely LTs, $V_{\text{O}}^{\times}$ that captures two electrons around it is assumed to exist, whereas the presence has never been reported as a majority.^{22),27)} For BaTiO₃, $V_{\text{O}}^{\bullet\bullet}$ has proven to be the major vacancy in the wide temperature range even at room temperature, indicating that the concentration of $V_{\text{O}}^{\bullet}$, [$V_{\text{O}}^{\bullet}$], is orders of magnitude lower than that of $V_{\text{O}}^{\bullet\bullet}$, [$V_{\text{O}}^{\bullet\bullet}$].^{22),25),26)} For SrTiO₃, $V_{\text{O}}^{\bullet}$ plays an important role in defect-related properties at LTs. It is indicated that $V_{\text{O}}^{\bullet}$ is the majority at room temperature;¹¹⁰⁾ the situation of [$V_{\text{O}}^{\bullet}$] > [$V_{\text{O}}^{\bullet\bullet}$] occurs below 550 °C¹¹¹⁾ and is maintained down to extremely LTs.¹¹²⁾ Other papers^{21),27),113)} report that [$V_{\text{O}}^{\bullet}$] is still much lower than [$V_{\text{O}}^{\bullet\bullet}$] at above room temperature. Saraf et al.¹¹⁴⁾ clearly show that the acceptor (Fe) doped SrTiO₃ in the p-type region have a high [$V_{\text{O}}^{\bullet}$] (10¹⁶–10¹⁸/cm⁻³) by over five orders of magnitude compared with [$V_{\text{O}}^{\bullet}$] (below ~10¹³/cm⁻³) while the donor (Nb) doped one in the n-type region displays extremely low concentrations (below ~10⁸/cm⁻³) of [$V_{\text{O}}^{\bullet}$] and [$V_{\text{O}}^{\bullet\bullet}$], the majority of which is dependent on an equilibrium condition.

2.3 Defect species

Table 1 lists the representative defects in BaTiO₃. Not only the Ba site but also the Ti site accommodates acceptors and donors as well as neutral dopants. On the Ba site, potassium ion (K⁺) acts as an acceptor, K_{Ba}[′], while lanthanum ion (La³⁺) plays a role of donor, La_{Ba}[•]. Strontium ion (Sr²⁺) can be positioned as Sr_{Ba}[×]; the *T_C* monotonically decreases with increasing [Sr_{Ba}[×]]. It is interesting to note that, depending on a boundary condition such as a starting chemical composition, Ca²⁺ occupies both on the Ba site (Ca_{Ba}[×])¹¹⁵⁾ and on the Ti site (Ca_{Ti}[′])^{116),117)} as is described later.

On the Ti site, wide variety of transition metal cations play a role of acceptor; one of the cations providing a

Table 1. Representative intrinsic point defects, acceptors, donors, and neutral defects in BaTiO₃. RE denotes RE elements (La, Nd, Sm, Dy, Ho, etc.) and TM indicates 3d-transition metal elements

Site	Acceptor	Neutral	Donor
Ba ²⁺	V _{Ba} ^{''} (vacancy) [†] , Li _{Ba} ['] (Li ⁺), Na _{Ba} ['] (Na ⁺), K _{Ba} ['] (K ⁺),	Ca _{Ba} [×] (Ca ²⁺), Sr _{Ba} [×] (Sr ²⁺), Pb _{Ba} [×] (Pb ²⁺), Sn _{Ba} [×] (Sn ²⁺) ^{††} , Pb _{Ba} [×] (Pb ²⁺),	RE _{Ba} [•] (RE ³⁺), Bi _{Ba} [•] (Bi ³⁺), Ce _{Ba} [•] (Ce ³⁺) ^{††}
Ti ⁴⁺	V _{Ti} ^{'''} (vacancy) [†] , Mg _{Ti} ^{''} (Mg ²⁺), Ca _{Ti} ^{''} (Ca ²⁺), Zn _{Ti} ^{''} (Zn ²⁺), TM _{Ti} ^{''} (TM ²⁺), Al _{Ti} ['] (Al ³⁺), Ga _{Ti} ['] (Ga ³⁺), In _{Ti} ['] (In ³⁺), TM _{Ti} ['] (TM ³⁺),	Sn _{Ti} [×] (Sn ⁴⁺), TM _{Ti} [×] (TM ⁴⁺), Zr _{Ti} [×] (Zr ⁴⁺), Hf _{Ti} [×] (Hf ⁴⁺), Ce _{Ti} [×] (Ce ⁴⁺) [†] ,	V _{Ti} [•] (V ⁵⁺) [†] , Nb _{Ti} [•] (Nb ⁵⁺), Ta _{Ti} [•] (Ta ⁵⁺), W _{Ti} [•] (W ⁶⁺) [†] , Mo _{Ti} [•] (Mo ⁵⁺) ^{††} , Mo _{Ti} [•] (Mo ⁶⁺) [†] ,
O ²⁻	N _O ['] (N ³⁻)	—	F _O [•] (F ⁻) V _O [•] V _O ^{••}

[†]These cation vacancies are minority defects, the concentrations of which are several orders of magnitude smaller than those of impurities even for undoped ones.²²⁾

^{††}The solubility is reported to be 5 % for (Ba_{0.87}Ca_{0.13})TiO₃.¹²²⁾

[†]The solubility limit is as small as several percent^{123),124)} or up to 20 %.¹²⁵⁾

^{††}The solubility limit is as small as several percent.¹²⁴⁾

[†]The doping effect is reported in the paper¹²⁶⁾ and the solubility limit in Bi₄Ti₃O₁₂ is up to several percent.¹⁰²⁾

[†]The solubility limit cannot be read in the paper.¹²⁷⁾

^{††}It is reported for reduced crystals.¹²⁸⁾

[†]It is speculated for oxidized crystals¹²⁸⁾ but that in Bi₄Ti₃O₁₂ is up to several percent.¹⁰⁶⁾

major impact is Fe³⁺ (Fe_{Ti}['],^{22),25)} because Fe cannot be perfectly removed from the Ti-containing raw materials such as TiO₂.^{22),26)} Therefore, Fe ions are inevitably involved as an unintentional impurity and often governs the overall behavior of undoped BaTiO₃.²²⁾ In contrast, higher valent cations such as Nb⁵⁺ and Ta⁵⁺ act as a donor,¹¹⁸⁾ Nb_{Ti}[•] and Ta_{Ti}[•], where Nb_{Ti}[•] has been widely used for decreasing [V_O^{••}].¹⁷⁾ On the O site, N³⁻ (N_O[']) has been recently demonstrated as an important anionic substituent,¹¹⁹⁾ because the T_C of BaTiO₃ can be possibly raised by increasing [N_O[']]. For the single crystals of BaTiO₃ grown by using KF as a flux, F⁻ (F_O[•]) is accompanied by K_{Ba}['], where the charge neutrality is satisfied through [F_O[•]] ≈ [K_{Ba}[']].^{120),121)}

2.4 Formalism

Unless otherwise stated, throughout this review, acceptor (A) doped BaTiO₃ is focused, where A is assumed to a variable-valence transition-metal (TM = Mn) cation on the Ti site; e.g., Mn²⁺ (Mn_{Ti}^{''}), Mn³⁺ (Mn_{Ti}[']), and Mn⁴⁺ (Mn_{Ti}[×]).^{26),114),129)} For generalization, the TM ions are expressed as A_{Ti}^{''}, A_{Ti}['], and A_{Ti}[×]. This formalism can be easily extended for fixed-valence acceptors such as Al³⁺, Mg²⁺ and Ca²⁺.^{22),23),28),130)}

The concentration of A remains constant regardless of a heating or cooling, as assumed in the literature;^{114),129)–132)}

the total concentration of A is unchanged (m_A is dosage of A):

$$m_A = [A_{Ti}'] + [A_{Ti}'] + [A_{Ti}^{\times}]. \quad (1)$$

The charge neutrality condition is expressed as

$$2[A_{Ti}'] + [A_{Ti}'] + n = 2[V_O^{\bullet\bullet}] + p, \quad (2)$$

where n and p are the concentrations of e' and $h^{\bullet}$, respectively. The equilibrium of thermally activated $e'-h^{\bullet}$ generation through band gap (E_g) can be written as

$$null \leftrightarrow e' + h^{\bullet}. \quad (3)$$

The product of n and p is equal to the intrinsic constant $K_I(T)$ as

$$\begin{aligned} K_I(T) &= n \cdot p \\ &= N_C(T) \cdot N_V(T) \exp\{-[E_g(0K) - \beta T]/kT\}, \end{aligned} \quad (4)$$

where $N_C(T)$ and $N_V(T)$ are the effective densities of states in the conduction band and the valence band, respectively²⁷⁾ and k the Boltzmann constant, $E_g(0K)$ the band gap at 0K^{36),37)} and β its temperature coefficient.¹¹⁰⁾ The formation of $V_O^{\bullet\bullet}$ by the oxygen kinetics is written as

and the mass-action constant of this reduction reaction (K_{Red}) is denoted as

$$K_{Red} = [V_O^{\bullet\bullet}]pO_2^{1/2}n^2 = K_{Red}^{\circ} \exp(-\Delta H_{Red}/kT), \quad (6)$$

where K_{Red}° indicates the temperature-independent one, and ΔH_{Red} the reduction enthalpy. In a similar manner as E_g , a T -dependent $\Delta H_{Red} = \Delta H_{Red}(0K) - \gamma T$ is adopted, which is slightly modified from the reported values.²⁷⁾

The ionization reactions of A on the Ti⁴⁺ site can be described by the generations either of e' or $h^{\bullet}$, while these are exactly identical.^{22),23),117),118),133)–135)} Here, the expressions based on the $h^{\bullet}$ generation are adopted. By producing $h^{\bullet}$, A ions can be ionized negatively, and the ionizations of A ions are expressed as:

where their respective equilibrium constants (K_{h1} and K_{h2}) and enthalpies (ΔH_{h1} and ΔH_{h2}) hold

$$K_{h1} = p[A_{Ti}']/[A_{Ti}'] = K_{h1}^{\circ} \exp(-\Delta H_{h1}/kT), \quad (9)$$

$$K_{h2} = p[Fe_{Ti}']/[Fe_{Ti}^{\times}] = K_{h2}^{\circ} \exp(-\Delta H_{h2}/kT). \quad (10)$$

where $K_{h1}^{\circ} = N_V(T)$ and $K_{h2}^{\circ} = N_V(T)$ are their respective equilibrium constants.²⁷⁾ Because E_g is temperature dependent, ΔH_{h1} and ΔH_{h2} also depend on temperature: $\Delta H_{h1} = \Delta H_{h1}(0K) - \beta T$ and $\Delta H_{h2} = \Delta H_{h2}(0K) - \beta T$, which are employed from the reported parameters.^{27),114),129)}

2.5 Relation among the enthalpies though E_g

The formulation described above is sufficient for calculating all the concentrations of majority/minority defect species, while the enthalpy diagram shown in **Fig. 3** enables us to understand the relation among the enthalpies that

Fig. 3. Schematic of the electronic band structure involving two redox potentials (A_{Ti}''/A_{Ti}' and A_{Ti}^x/A_{Ti}') of $BaTiO_3$ along with the enthalpies of defect related reactions. Sums of hole-generation enthalpies (ΔH_{h1} and ΔH_{h2}) and electron-generation ones (ΔH_{e1} and ΔH_{e2}) are equal to the band gap (E_g). The enthalpies of the oxidation reactions (ΔH_{Ox1} and ΔH_{Ox2}) and the reduction reaction (ΔH_{Red}) are also connected through E_g .

are connected through E_g . This is because the thermally activated $e'-h^*$ creation is divided by the hole generation reactions [Eqs. (9) and (10)] and the electron generation reactions [Eqs. (11) and (12)], where the redox potentials of A_{Ti}''/A_{Ti}' and A_{Ti}^x/A_{Ti}' act as stepping stones. These redox potentials are located inside E_g , the energy gap between the Ti-3d derived conduction band and the O-2p derived valence band. The electron generation reactions from A'' and A' are given as

where K_{e1} and K_{e2} denote their respective equilibrium constants, and ΔH_{e1} and ΔH_{e2} their respective enthalpies.^{136,137} Because the sums of Eqs. (7) and (11) as well as Eqs. (8) and (12) give $null \leftrightarrow e' + h^*$, the following relations arise:

$$\Delta H_{e1} + \Delta H_{h1} = E_g, \quad (13)$$

$$\Delta H_{e2} + \Delta H_{h2} = E_g. \quad (14)$$

The oxygen-incorporation reaction accompanied by the valence change of A'' into A' is written as

$$K_{Ox1} = [A']^2 \{ [A'']^2 pO_2^{1/2} [V_O^{\bullet\bullet}] \}^{-1}, \\ = K'_{Ox1} \exp(-\Delta H_{Ox1}/kT). \quad (16)$$

In a similar manner, the reaction with A' into A^x is given as

$$K_{Ox2} = [A^x]^2 \{ [A']^2 pO_2^{1/2} [V_O^{\bullet\bullet}] \}^{-1}, \\ = K'_{Ox2} \exp(-\Delta H_{Ox2}/kT), \quad (18)$$

where their respective equilibrium constants and enthalpies are indicated in parenthesis. Using Eqs. (3), (6) and (9), the following relation is given:

Fig. 4. Experimental and calculated equilibrium conductivity isotherms for undoped $BaTiO_3$ (ceramics).²²⁾ Symbols represent experimental points, whereas solid lines are calculated from proposed defect model; dashed lines illustrate ideal slopes. (●) Calculated conductivity considering only electrons and holes (1 MPa = 9.87 atm). Reprinted with permission from Chan N-H et al. *J. Am. Ceram. Soc.* 1981;64(9):556–562. Copyright 1981 American Ceramic Society/Wiley Publishing.

$$2E_g = \Delta H_{Red} + \Delta H_{Ox1}. \quad (19)$$

Also, Eqs. (3), (6) and (10) derive the following relation:

$$2E_g = \Delta H_{Red} + \Delta H_{Ox2} (\Delta H_{Ox1} = \Delta H_{Ox2}). \quad (20)$$

Note that the ΔH_{Ox1} and ΔH_{Ox2} have negative values, as indicated in Fig. 3.

This is consistent with the fact that the reactions of an oxygen incorporation into the lattice of Eqs. (15) and (17) proceed with decreasing temperature; $[V_O^{\bullet\bullet}]$ decreases when an equilibrium temperature is lowered.^{136,137}

2.6 HT equilibrium states

Figure 4 shows the conductivity data of undoped $BaTiO_3$ ceramics reported by the Smyth's group.²²⁾ The data in a whole range of pO_2 was presented with a help of a calcia-stabilized zirconia cell as an electrochemical oxygen leak or pump to modify pO_2 . They revealed that the conductivity behavior can be completely explained by considering only the defect species of $V_O^{\bullet\bullet}$, A' (e.g., trivalent acceptor on the Ti site), e' and h^* . Namely, it was demonstrated that the defect chemistry is governed by unintentional acceptor impurities and also that the intrinsic cation vacancies (V_{Ba}'' and V_{Ti}'''')^{138,139} play a minor role.

In the higher pO_2 regime, the p-type conduction prevails with its conductivity $\sigma_p \propto p \propto pO_2^{1/4}$, where the charge neutrality condition is $[A'] \approx 2[V_O^{\bullet\bullet}]$. In the lower pO_2 regime, the n-type conduction is dominant with its conductivity of $\sigma_n \propto n \propto pO_2^{-1/4}$ ($[A'] \approx 2[V_O^{\bullet\bullet}]$) at the intermediate pO_2 and $n \propto pO_2^{-1/6}$ ($n \approx 2[V_O^{\bullet\bullet}]$) at the extremely low pO_2 . It is worth noting that the data near the conductivity minimum are apparently higher than the extrapolated lines of $\sigma_p \propto pO_2^{1/4}$ and $\sigma_n \propto pO_2^{-1/4}$. These discrepancies are explained by oxide-ion (O^{2-}) conduction, whose activation energy was determined to be 1.1 eV.

They also reported the conductivity data of undoped $BaTiO_3$ ceramics with different Ba/Ti compositions along

with single crystals.²²⁾ Regardless of the Ba/Ti compositions or the bulk form (polycrystal or single crystal), the HT conductivities accord well with each other. If the composition of Ba/Ti = 0.995 were assumed to provide Ti vacancies, its concentration $[V_{\text{Ti}}^{''''}]$ is of the order of thousand ppm. It should lead to conductivities several orders of magnitude higher than those of Ba/Ti = 1.000. Moreover, the almost the same conductivities for polycrystals and single-crystals revealed that the point defects ($V_{\text{O}}^{\bullet\bullet}$, A' , e' and $h^{\bullet}$) govern the conductivity behavior and also that the motilities of e' and $h^{\bullet}$, i.e., the electronic carrier scattering at grain boundaries play a minor role. These results lead to the conclusion that acceptors involved unintentionally in raw materials govern the defect chemistry.

Using the thermodynamic data set involving temperature-dependent band gap, mass-action constants, enthalpies of redox couples etc., all the equilibrium concentrations of defects including electronic carriers (electron and hole) could be quantitatively calculated,^{(129),(140),(141)} and the HT properties such as electrical conductivities, thermopowers and Seebeck coefficients were unambiguously explained.^{(27),(110),(111),(142),(143)}

2.7 LT quenched states

At HTs, e.g., at above 900 °C, the kinetics of oxygen exchange between oxides and the surrounding gas phase is relatively fast.^{(132),(137)} The oxygen activity inside the samples can be regarded as in an equilibrium state. Afterwards, this framework is extended to the LT defect chemistry in quenched states;^{(28),(29),(113),(114),(130),(144)–(146)} the total oxygen vacancy concentration in the HT equilibrium states ($[V_{\text{O}}^{\bullet\bullet}] + [V_{\text{O}}^{\bullet}]$) is assumed to be frozen-in at LTs, because of a sufficiently low mobility of oxide ions. In a meanwhile, an oxygen-reaction kinetics at surfaces and/or interfaces that is a bridge between the HT-equilibrium and the LT-quenched states was intensively studied, which is described in detail in the review paper.⁽¹⁴⁷⁾

When the temperature is lowered, the long-range ionic motion fails to reach its equilibrium. At LTs below 400 °C,⁽¹⁴²⁾ it can be assumed that $[V_{\text{O}}^{\bullet\bullet}] + [V_{\text{O}}^{\bullet}]$ in the HT equilibrium state is frozen-in because the oxygen exchange kinetics is extremely slow.^{(28),(114),(132),(136),(147)} The reaction involving oxygen incorporation or release expressed by Eq. (5) does not occur, whereas the internal electronic reactions of the bandgap excitation (3) and the electron-trapping reactions of A ions ([7] and (8)) are still active even at LTs.^{(28),(114),(132),(136),(147)}

Figure 5 shows the schematic defect diagram for acceptor (Ni)-doped SrTiO₃ in a HT (727 °C) equilibrium and a LT (227 °C) quenched states. In this figure, the extremely low p_{O_2} regime ($n \approx 2[V_{\text{O}}^{\bullet\bullet}]$) is not taken into account. In the almost entire p_{O_2} range, the charge neutrality condition is $[A''] \approx [V_{\text{O}}^{\bullet\bullet}]$ ($A = \text{Ni}$), regardless of the HT or LT state. In the HT state, the majority carrier concentrations have the following formulae $p_{\text{HT}} \propto p_{\text{O}_2}^{1/4}$ in the higher p_{O_2} regime and $n_{\text{HT}} \propto p_{\text{O}_2}^{-1/4}$ in the lower p_{O_2} one, whose ‘V-shaped’ behavior is essentially the same as that in Fig. 4. In the LT state, the following two features appear: one is

Fig. 5. Schematic defect diagram for acceptor-doped SrTiO₃ during equilibrium at 727 °C (thin lines, indices: HT) and after quenching at 727 °C (thick lines, indices: LT) as a function of the oxygen partial pressure during equilibration, $p_{\text{O}_2}^{\text{Eq}}$.⁽¹¹³⁾ Defect concentration labels without HT and LT indices remain virtually unchanged during quenching. Mass action constants are taken from the collection in the paper⁽¹⁴¹⁾ except that a concentration of 0.8 at % of an acceptor with an ionization energy $\Delta H_{h1} = 1$ eV was assumed for the calculation: (—) electron and hole concentrations, (· · ·) oxygen vacancy concentration, (---) doubly ionized acceptor, (---) singly ionized acceptor. Reprinted with permission from Waser R. *J. Am. Ceram. Soc.* 1991;74(8):1934–1940. Copyright 1991 American Ceramic Society/Wiley Publishing.

$n_{\text{HT}} \approx n_{\text{LT}}$, exhibiting that there exists no trap for e' , and the other is $p_{\text{HT}} \gg p_{\text{LT}}$ that is derived from a hole trap by A'' .

Waser also reported the schematic conductivity diagram for acceptor (Ni)-doped SrTiO₃ in the LT quenched state after equilibration.⁽¹¹³⁾ With decreasing p_{O_2} , the majority carrier changes from $h^{\bullet}$, O^{2-} ($V_{\text{O}}^{\bullet\bullet}$), to e' , and thereby the dominant conduction mechanism also changes from hole conduction (total conductivity $\sigma_{\text{tot}} \approx \sigma_{h^{\bullet}}$), oxide-ion conduction ($\sigma_{\text{tot}} \approx \sigma_{V_{\text{O}}^{\bullet\bullet}} = \sigma_{\text{O}^{2-}}$) to electron conduction ($\sigma_{\text{tot}} \approx \sigma_{e'}$). As explained above, the redox couple A'/A'' ($\text{Ni}^{3+}/\text{Ni}^{2+}$) acts as a trap for $h^{\bullet}$, and its conductivity is relatively low with the relation of $p_{\text{LT}} \propto p_{\text{O}_2}^{1/4}$. In the intermediate p_{O_2} regime, $\sigma_{V_{\text{O}}^{\bullet\bullet}}$ prevails and does not depend on p_{O_2} , because $[V_{\text{O}}^{\bullet\bullet}]$ remains constant ($[A''] \approx [V_{\text{O}}^{\bullet\bullet}]$). At low p_{O_2} , $\sigma_{e'}$ is dominant and its value is up to four orders of magnitude higher than p_{LT} . This high $\sigma_{e'}$ is attributed to a high n_{LT} arising from an absence of effective trap for e' .

3. Defect concentration calculations

The details of the calculations are described in our preceding paper⁽²⁹⁾ and the references therein. The calculation procedure is as follows: first, the defect concentrations in the HT state, e.g., at 900 °C are calculated as a function of $p_{\text{O}_2}^{\text{HT}}$; next, under the fixed value of $[V_{\text{O}}^{\bullet\bullet}]$ at each $p_{\text{O}_2}^{\text{HT}}$, all the other concentrations in the LT quenched state are calculated as a function of T .

3.1 Ba(Ti,Ca)O₃

As described above, Ca^{2+} can be positioned both on the Ba site ($\text{Ca}_{\text{Ba}}^{\times}$)⁽¹¹⁵⁾ and on the Ti site ($\text{Ca}_{\text{Ti}}^{\prime\prime}$),^{(116),(117)} which depends on the boundary condition such as the

Fig. 6. Defect concentration diagram for $\text{Ba}(\text{Ti}_{1-x}\text{Ca}_x)\text{O}_3$ ($x = 0.005$) in an equilibrium state at 900°C . The horizontal axis is the $p\text{O}_2$ at 900°C and the vertical axis is the defect concentrations in the linear scale (a), (b) and in the logarithmic scale (c).

composition. Here, the role of Ca as an acceptor, Ca_{Ti}'' , is focused. For the calculations, the hole generation enthalpy $[\Delta H_h = \Delta H_h(0\text{ K}) - \beta T]$ of the following reaction is required, which is reported to be 0.54 eV in the temperature range of $827\text{--}977^\circ\text{C}$.¹⁴⁸⁾

It should be emphasized that Ca_{Ti}' is regarded not as Ca^+ but as Ca^{2+} that captures $h^\bullet$, i.e., $h^\bullet$ is trapped around Ca^{2+} as a defect complex of $\text{Ca}^{2+}\text{--}h^\bullet$ because of a crystallographic potential on the Ti^{4+} site.^{22,23)} $\Delta H_h(0\text{ K})$ is set to be 1.0 eV , which leads to a $\Delta H_h(1,173\text{ K})$ of 0.57 eV at $\beta = 3.7 \times 10^{-4}\text{ eV K}^{-1}$.

Figure 6 shows the defect concentration diagram of $\text{Ba}(\text{Ti}_{1-x}\text{Ca}_x)\text{O}_3$ ($x = 0.005$) in the HT (900°C) equilibrium state. The total Ca concentration is fixed to be 0.5% corresponding to $1.55 \times 10^{20}\text{ cm}^{-3}$; the majority is Ca_{Ti}'' ($[\text{Ca}_{\text{Ti}}''] \approx [\text{V}_{\text{O}}^{\bullet\bullet}]$ except at an extremely low $p\text{O}_2$); $[\text{Ca}_{\text{Ti}}']$ is orders of magnitude higher than $[\text{Ca}_{\text{Ti}}']$. With decreasing $p\text{O}_2$ from 1 atm , $\text{V}_{\text{O}}^{\bullet\bullet}$ is indeed generated, where the charge neutrality is satisfied by a decrease in $[\text{Ca}_{\text{Ti}}']$, see Eq. (7). In this regime, the electronic carrier is $h^\bullet$ (p-type) which is detrapped in a thermally activated process with ΔH_h . A carrier crossover appears at $p\text{O}_2 \sim 10^{-8}\text{ atm}$, where e' prevails over $h^\bullet$; the electronic conduction changes from p-type to n-type, delivering a ‘V-shaped’ conductivity.¹¹⁷⁾ With further decreasing $p\text{O}_2$, the charge balance is maintained by Eq. (5). At below $p\text{O}_2 < 10^{-27}\text{ atm}$, the charge neutrality condition is approximated as $n \approx 2[\text{V}_{\text{O}}^{\bullet\bullet}]$ with $n \propto p\text{O}_2^{-1/6}$.

Figure 7 shows the defect concentration diagram of $\text{Ba}(\text{Ti}_{1-x}\text{Ca}_x)\text{O}_3$ ($x = 0.005$) in the LT (25°C) quenched state. Note that the $p = [h^\bullet]$ in the high $p\text{O}_2$ region is as low as $10^2\text{--}10^5\text{ cm}^{-3}$ that leads to a p-type insulation while the $n = [e']$ in the low $p\text{O}_2$ region is high over 10^{15} cm^{-3} that results in an n-type semiconduction. This is similar to

Fig. 7. Defect concentration diagram for $\text{Ba}(\text{Ti}_{1-x}\text{Ca}_x)\text{O}_3$ ($x = 0.005$) at 25°C after equilibration at 900°C along with an electronic conduction behavior. The $[\text{V}_{\text{O}}^{\bullet\bullet}]$ values equilibrated at 900°C is assumed to be frozen-in and thereby the horizontal axis denotes $p\text{O}_2$ at 900°C .

the conduction diagram for Ni-doped SrTiO_3 ceramics¹¹³⁾ (actually, oxide-ion conduction $\sigma_{\text{O}^{2-}}$ prevails over hole conduction $\sigma_{h^\bullet}$ in the intermediate $p\text{O}_2$). The p-type insulation is achieved by a trap of $h^\bullet$ by the $\text{Ca}_{\text{Ti}}'/\text{Ca}_{\text{Ti}}''$ redox couple. In contrast, the n-type semiconduction is due to no trap for e' : the high n in the HT state is maintained in the LT state. The transition $p\text{O}_2$ between the high-resistivity p-type insulation and the n-type semiconduction ($p\text{O}_2^{n-p}$) is lowered by increasing $[\text{A}_{\text{Ti}}']$, which is expressed as

$$d \log p\text{O}_2^{n-p} / d \log [\text{A}_{\text{Ti}}'] = -2. \quad (22)$$

3.2 $\text{Ba}(\text{Ti,Mn})\text{O}_3$

The valence state of Mn on the Ti site varies among Mn^{2+} (Mn_{Ti}''), Mn^{3+} (Mn_{Ti}'), and Mn^{4+} ($\text{Mn}_{\text{Ti}}^{\times}$).^{4),25),28),129),136),149),150)} Hagemann and Hennings have reported the hole generation enthalpy ΔH_{h1} (1.87 eV) associated with the redox reaction of $\text{Mn}_{\text{Ti}}'/\text{Mn}_{\text{Ti}}''$ and the ΔH_{h2} (1.28 eV) with that of $\text{Mn}_{\text{Ti}}^{\times}/\text{Mn}_{\text{Ti}}''$ in the temperature range of $800\text{--}1,200^\circ\text{C}$. The $\Delta H_{h1}(0\text{ K})$ of 2.30 eV and the $\Delta H_{h2}(0\text{ K})$ of 1.71 eV are adopted along with $\beta = 3.7 \times 10^{-4}\text{ eV K}^{-1}$, corresponding to $\Delta H_{h1}(900^\circ\text{C}) = 1.87\text{ eV}$ and $\Delta H_{h2}(900^\circ\text{C}) = 1.23\text{ eV}$.

Figure 8 shows the defect concentration diagram of $\text{Ba}(\text{Ti}_{1-x}\text{Mn}_x)\text{O}_3$ ($x = 0.001$) in an HT (900°C) equilibrium state. Note that with decreasing $p\text{O}_2$ from 1 atm the majority of Mn ion changes from Mn^{4+} , Mn^{3+} to Mn^{2+} . In the higher $p\text{O}_2$ region at above 10^{-5} atm , the charge neutrality condition is expressed as $[\text{Mn}_{\text{Ti}}'] \approx 2[\text{V}_{\text{O}}^{\bullet\bullet}]$. An increase in $p\text{O}_2$ oxidizes Mn_{Ti}' to $\text{Mn}_{\text{Ti}}^{\times}$ and thereby $[\text{V}_{\text{O}}^{\bullet\bullet}]$ is reduced. In the intermediate $p\text{O}_2$ region of $10^{-15}\text{--}10^{-5}\text{ atm}$, the charge neutrality condition is $2[\text{Mn}_{\text{Ti}}'] + [\text{Mn}_{\text{Ti}}^{\times}] \approx 2[\text{V}_{\text{O}}^{\bullet\bullet}]$. With decreasing $p\text{O}_2$ further, the charge neutrality condition changes from $n + 2[\text{Mn}_{\text{Ti}}'] + [\text{Mn}_{\text{Ti}}^{\times}] \approx 2[\text{V}_{\text{O}}^{\bullet\bullet}]$ ($10^{-22}\text{--}10^{-15}\text{ atm}$) to $n \approx 2[\text{V}_{\text{O}}^{\bullet\bullet}]$ ($p\text{O}_2 < 10^{-22}\text{ atm}$). As to the electronic carrier, the ‘V-shaped’ character is seen, which is essentially the same as those displayed in Figs. 4 and 6(c), while two redox couples of $\text{Mn}_{\text{Ti}}^{\times}/\text{Mn}_{\text{Ti}}'$ and $\text{Mn}_{\text{Ti}}'/\text{Mn}_{\text{Ti}}''$ play a role, as indicated in Eqs. (9) and (10).

Figure 9 shows the defect concentration diagram of $\text{Ba}(\text{Ti}_{1-x}\text{Mn}_x)\text{O}_3$ ($x = 0.001$) in the LT (25°C) quenched

Fig. 8. Defect concentration diagram of $\text{Ba}(\text{Ti}_{1-x}\text{Mn}_x)\text{O}_3$ ($x = 0.001$) in a HT (900 °C) equilibrium state. The vertical axis is the defect concentrations in the linear scale (a) and in the logarithmic scale (b).

Fig. 9. Defect concentration diagram for $\text{Ba}(\text{Ti}_{1-x}\text{Mn}_x)\text{O}_3$ ($x = 0.001$) at 25 °C after equilibrium at 900 °C along with an electronic conduction behavior and the majority Mn valence. The $[V_O^{\bullet\bullet}]$ values equilibrated at 900 °C is assumed to be frozen-in and thereby the horizontal axis denotes p_{O_2} at 900 °C.

state. With decreasing p_{O_2} , there exists two distinct thresholds: one is $p_{\text{O}_2}^{n-p}$ at which a carrier crossover between p-type and n-type occurs, and the other is $p_{\text{O}_2}^{S-I}$ at which a transition from an n-type insulation to an n-type semiconduction. Even though the Mn content is as low as 0.1 %, the p_{O_2} with an insulating feature is extended down to 10^{-17} atm.

At $p_{\text{O}_2} > p_{\text{O}_2}^{n-p}$, the $\text{Mn}_{\text{Ti}}^{\times}/\text{Mn}_{\text{Ti}}^{\cdot'}$ couple acts as a trap for $h^{\bullet}$ as expressed by Eq. (9), leading to a p-type insulation. This is consistent with the extremely high resistance observed for Mn-doped ceramics.¹³⁶⁾ In the intermediate p_{O_2} ($p_{\text{O}_2}^{S-I} > p_{\text{O}_2} > p_{\text{O}_2}^{n-p}$) the redox reaction owing to $\text{Mn}_{\text{Ti}}^{\cdot'}/\text{Mn}_{\text{Ti}}^{\cdot''}$ can trap e' and thereby the n-type insulation is seen; the n is below 10^2 cm^{-3} , which is orders of magnitude lower than that in Ca-doped BaTiO_3 (see Fig. 7). At below $p_{\text{O}_2}^{S-I}$, the n is extremely high, leading to an n-type semiconduction, as displayed in Fig. 7.

Figure 10 shows the evolution of the defect concentration diagram of $\text{Ba}(\text{Ti}_{1-x}\text{Mn}_x)\text{O}_3$ ($x = 0.001$) in the LT

Fig. 10. Evolution of the defect concentration diagram of $\text{Ba}(\text{Ti}_{1-x}\text{Mn}_x)\text{O}_3$ ($x = 0.001$) in the LT (25 °C) state with respect to different equilibrium temperature (T^{eq}). The $[V_O^{\bullet\bullet}]$ values equilibrated at T^{eq} is assumed to be frozen-in and thereby the horizontal axis denotes p_{O_2} at 900 °C.

(25 °C) state with respect to different equilibrium temperature (T^{eq}). With decreasing T^{eq} , the following features appear: I. the oxygen incorporation reactions of Eqs. (15) and (17) proceed and then $[V_O^{\bullet\bullet}]$ decrease because of the negative ΔH_{Ox1} and ΔH_{Ox2} ; II. the Mn^{4+} and Mn^{3+} majority regions are widened; III. the $p_{\text{O}_2}^{S-I}$ and $p_{\text{O}_2}^{n-p}$ thresholds decrease monotonically, i.e., the insulation region is spread down to $p_{\text{O}_2} \approx 10^{-26}$ atm at $T^{\text{eq}} = 700$ °C. For the ceramics doped with variable valence acceptors such as Mn, a LT annealing followed by a HT sintering is effective not only for decreasing $[V_O^{\bullet\bullet}]$ but also for obtaining high-insulation resistances.⁴⁾

4. Functions derived from defect control

Functions of TM oxides are strongly associated with the valence state(s) of TM cations and their wavefunctions mixed with O-2p. For $(\text{La},\text{Sr})\text{MnO}_{3-\delta}$ and its related perovskites, the coexistence of Mn^{3+} and Mn^{4+} provides various spin-derived functions such as magnetic orders colossal magnetoresistances, metal-insulator transitions.^{151)–155)} For BaTiO_3 , TM (Mn, Fe, etc.) cations generate electron-filled and/or empty states inside E_g . Here, I describe that the coexistence of Fe^{2+} and Fe^{3+} whose concentrations are the same order offers unprecedented PV effect in BaTiO_3 ; the Fe^{2+} -derived donor state and the Fe^{3+} -derived acceptor state act as robust scaffolds for generating $e'-h^{\bullet}$ pairs under visible light.²⁹⁾

4.1 Bulk PV effect

The polar lattice with spatial inversion symmetry breaking arises in the bulk PV effect^{13),156),157)} associated with

Fig. 11. Defects states in Fe-doped BaTiO₃.²⁹⁾ **a, b** Electronic configurations in the high spin state of Fe³⁺ and Fe²⁺ in O_h symmetry. **c, d** Gap states derived from Fe²⁺ and Fe³⁺ in the bandgap (E_g) between the conduction band (Ti-3d) and the valence band (O-2p) in the host BaTiO₃ lattice. **e** Defect concentrations at 25 °C as a function of oxygen partial pressure ($P_{O_2}^{900^\circ\text{C}}$) at 900 °C (annealing temperature). In the region III, photoinduced carriers are expected to be generated as follows: the unoccupied t_{2g} state of Fe³⁺ **c** is positioned above the VBM (the top of the O-2p band) and then play the role of an electron acceptor, while the electron-occupying t_{2g} state of Fe²⁺ **d** is located below the CBM (the bottom of the Ti-3d band) and then acts as an electron donor. Reprinted from Noguchi Y. *Nat. Commun.* 2020;11(1):1–10. Copyright 2020 Nature Publishing Group.

high voltages beyond the bandgap limit of semiconductor p-n junctions.^{156)–159)} The ferroelectric PV effect appears under ultraviolet light for wide-bandgap oxides such as LiNbO₃,^{156),160),161)} BaTiO₃,^{11),12),162)–164)} and BiFeO₃.^{158),159),165)} The poor absorption of visible light is improved by band-gap narrowing,^{166)–170)} which is accompanied by a substantial decrease in P_s . Gap-state engineering employing mid-gap states for BiFeO₃¹⁷¹⁾ can enhance photocurrents without sacrificing photovoltages, where the photon energy of at least half of E_g is required.

4.2 Strategy for visible-light activation

Owing to the high E_g of BaTiO₃ (3.2 to 3.3 eV),^{172),173)} the PV effect arises under ultraviolet light. To activate a visible-light response, electronic states derived from Fe²⁺ and Fe³⁺ are introduced into the bandgap, and these gap states are utilized as scaffolds for carrier generation.

In O_h symmetry (**Figs. 11a** and **11b**), Fe³⁺ (d^5) in the high spin state has $t_{2g}^3(\text{up}) e_g^2(\text{up}) t_{2g}^0(\text{down}) e_g^0(\text{down})$ and Fe²⁺ (d^6) $t_{2g}^3(\text{up}) e_g^2(\text{up}) t_{2g}^1(\text{down}) e_g^0(\text{down})$. In the BaTiO₃, the $t_{2g}^3(\text{up}) e_g^2(\text{up})$ states appear near the bottom of the valence band,¹⁷⁴⁾ while the $t_{2g}^0(\text{down})$ states of Fe³⁺ (**Fig. 11c**) and the $t_{2g}^1(\text{down})$ one of Fe²⁺ (**Fig. 11d**) are positioned inside the bandgap. Therefore, the following strategy for generating e^-h^+ pairs under visible light is inspired: Fe³⁺ offers an electron acceptor leading to hole injection into the valence band,^{175),176)} and Fe²⁺ provides an electron donor resulting in electron injection into the conduction band.^{177)–179)} In the coexisting state of Fe³⁺ and Fe²⁺, e^-h^+ pairs can be generated at photon energy ($h\nu$) much smaller than E_g . Here, the Fe-3d derived states without an asterisk, such as t_{2g} and d_{xy} , are the bonding

Fig. 12. DFT energies of Fe-doped BaTiO₃.²⁹⁾ The horizontal axis n denotes the $V_{On}^{\bullet\bullet}$ (oxygen vacancy)-site number in the tetragonal Ba₂₇Ti₂₆FeO₈₁ structures, and the vertical axis is the DFT energy with respect to that of $n = 1$ in the **a** Fe³⁺ and **b** Fe²⁺ cells. $V_O^{\bullet\bullet}$ is adjacent to iron atoms in the $n = 1$ to 3 cells and is away from iron atoms in the $n = 4$ to 21 cells, as illustrated in the insets of the $n = 1$ ($V_{O1}^{\bullet\bullet}$) and $n = 4$ ($V_{O4}^{\bullet\bullet}$) cells. Regardless of the valence state of iron, the energies with $n = 1$ to 3 are 0.6 to 0.8 eV lower than those with $n = 4$ to 21. These results show that $V_O^{\bullet\bullet}$ is attracted by iron and eventually stabilized on the O1 site (the NN site with Fe). Reprinted from Noguchi Y. *Nat. Commun.* 2020;11(1):1–10. Copyright 2020 Nature Publishing Group.

states, while those with asterisk (*), e.g., t_{2g}^* and d_{xy}^* , are the antibonding ones.

Figure 11e shows the defect concentration diagram at 25 °C as a function of $pO_2^{900^\circ\text{C}}$ in Fe (0.3 %)-doped BaTiO₃,²⁹⁾ where four regions exist. In the regions I and II, the majority of iron is trivalent, namely, $[\text{Fe}^{3+}]$ is orders of magnitude higher than others; the minority is Fe⁴⁺ at a higher P_{O_2} (I) and Fe²⁺ at a lower P_{O_2} (II). The region III is the coexisting state of Fe³⁺ and Fe²⁺, the concentrations of which have the same order. At the higher $pO_2^{900^\circ\text{C}}$ side (I, II, and III), the charge neutrality is $2[\text{Fe}_{\text{Ti}}'] + [\text{Fe}_{\text{Ti}}''] \approx 2[V_O^{\bullet\bullet}]$. The region IV is semiconducting with a high n , along with Fe²⁺ as the majority ($n \approx 2[V_O^{\bullet\bullet}]$). It is expected that the region III is capable of providing a robust PV response under visible light. Therefore, an $P_{O_2}^{900^\circ\text{C}}$ of 10^{-23} atm is adopted as an annealing condition, where the concentrations are calculated to be $[\text{Fe}_{\text{Ti}}'] \approx 3.5 \times 10^{19} \text{ cm}^{-3}$ and $[\text{Fe}_{\text{Ti}}''] \approx 4.3 \times 10^{19} \text{ cm}^{-3}$.

4.3 Defect associates

Figure 12 shows the density-functional theory (DFT) energy with n of $V_{On}^{\bullet\bullet}$, where $V_{On}^{\bullet\bullet}$ denotes the $V_O^{\bullet\bullet}$ on the n -th NN site with respect to Fe. The cells with $n = 1$ to 3 has small energies compared with others regardless of the Fe valence. It can be thought that an attractive interaction works between iron and $V_O^{\bullet\bullet}$. Because $V_O^{\bullet\bullet}$ has a certain mobility even below the T_C , $V_O^{\bullet\bullet}$ is trapped by Fe and is eventually positioned on the nearest-neighbour (NN) O1 site (**Figs. 13b** and **13c**) after a

Fig. 13. Crystal structures of tetragonal (T) Fe-BaTiO₃ cells.²⁹ The crystal structures optimized by DFT calculations are displayed for **a** Ba₂₇Ti₂₆FeO₈₁ (Fe³⁺), **b** Ba₂₇Ti₂₆FeO₈₀ (Fe³⁺-V_{O1}**), and **c** Ba₂₇Ti₂₆FeO₈₀ (Fe²⁺-V_{O1}**). The valence states of Fe are controlled by the total number of electrons. The crystal symmetry was converged in tetragonal space group *P4mm* for all the cells, where the spontaneous polarization (*P_s*) is parallel to the *c* axis. O1 and O3 are defined as the first and third NN oxygen atoms with respect to Fe in the defect-free cell. Ti1 is the first-NN titanium atom with Fe. In the defective cells, an oxygen vacancy (V_O**) is stabilized on the first NN O1 site, namely, is present as the associate of Fe³⁺-V_O** or Fe²⁺-V_O**. Reprinted from Noguchi Y. *Nat. Commun.* 2020;11(1):1–10. Copyright 2020 Nature Publishing Group.

certain period. In aged samples, V_O** exists as a defect associate of Fe³⁺-V_O** and/or Fe²⁺-V_O**.

The energy levels of the Fe-derived states can explain the formation of the defect associates. The orbital interactions provide bonding and antibonding states in both the majority (↑) and minority (↓) spin bands. In the ↑ band, the bonding states appear near the bottom of the valence band, and the antibonding states (marked with asterisk) arise near or inside the band gap (**Fig. 14**). For the Fe³⁺-V_{O1}** and Fe³⁺-V_{O4}** cells, the *t_{2g}** and *e_g** states are similar and their energy levels are close, while the *t_{2g}* and *e_g* states display different properties: these bonding states of the Fe³⁺-V_{O1}** cell are lower in energy by ≈0.5 eV than those of the Fe³⁺-V_{O4}** cell. The attractive interaction between Fe³⁺ and V_O** originates from these low-lying bonding states. As for Fe²⁺, the Fe²⁺-V_{O4}** cell has electron-filled gap states: the Fe-3*d_{xz}* state (↓) and the Fe-3*d_{yz}**, -3*d_{x²-y²}** and -3*d_{yz}** states in the ↑ band. In contrast, the Fe²⁺-V_{O1}** cell (Figs. 14e and 14f) has only two gap states of Fe-3*d_{z²}* (↓) and -3*d_{x²-y²}** (↑). The remaining ↑ states, namely, Fe-3*d_{xz}**, -3*d_{yz}**, -3*d_{xy}**, and -3*d_{z²}**, are located at lower energy and are near the valence band bottom. The stabilization of V_O** on the O1 site, i.e., the formation of the Fe²⁺-V_O** associate, arises from these lower-lying Fe-3*d* states.

Because a short-range V_O** motion with a distance of a few unit cells occurs even near room temperature,^{147),180)}

Fig. 14. Electronic structures of tetragonal (T) Fe-BaTiO₃.²⁹ Band structures and total (partial) density of states (DOS) for the **a**, **b** Fe³⁺, **c**, **d** Fe³⁺-V_{O1}**, and **e**, **f** Fe²⁺-V_{O1}** cells, where V_{O1}** denotes the oxygen vacancy on the O1 site. The Fermi level is indicated by *E_F*. In the band structure, the red and blue lines represent the majority (↑) and minority (↓) spin components, respectively. The valence band and the conduction band of the host BaTiO₃ lattice are coloured light blue and light orange, respectively. The bandgap is denoted by *E_g*. The red and blue arrows in **e** represent electrons occupying in their corresponding spin bands. In the DOS, the right and left panels correspond to the ↑ and ↓ bands, respectively, as indicated in the total DOS. The Fe³⁺ cell has the empty gap state of *t_{2g}* (bonding) in the ↓ band. In the Fe³⁺-V_O** and Fe²⁺-V_O** cells, the degeneracy of the *d* orbitals is lifted owing to the presence of V_O**. In the Fe³⁺-V_O** cell, four empty *d* (↓) states (bonding) appear near the middle of the bandgap. In the Fe²⁺-V_O** cell, the electron-occupied *d_{x²-y²}** (↑) state is above the VBM (asterisk denotes antibonding), and the *E_F* is formed near the middle of the bandgap by the occupied *d_{z²}* (↓) state (bonding). Reprinted from Noguchi Y. *Nat. Commun.* 2020;11(1):1–10. Copyright 2020 Nature Publishing Group.

it is reasonable to assume that all oxygen vacancies are present as the defect associates of Fe³⁺-V_O** and/or Fe²⁺-V_O** in the samples, as reported for SrTiO₃^{181),182)} and PbTiO₃^{183),184)} and BaTiO₃.^{185),186)}

4.4 Gap states of Fe-3*d*

Figure 14 shows the electronic structures of the Fe³⁺, Fe³⁺-V_O**, and Fe²⁺-V_O** cells (their crystal structures in Fig. 13). In **Fig. 15**, the defect levels for the Fe²⁺-V_{O1}** and Fe³⁺-V_{O1}** cells are schematized, where the corresponding wavefunctions of the Fe-3*d* derived gaps states are displayed. As reported in the literature,^{108),187)} the valence band is mainly formed by O-2*p*, while the conduction band is primarily composed of Ti-3*d*, where an orbital hybridization between them are present.

Fig. 15. Mechanism of the visible-light PV effect.²⁹⁾ The photoresponse of the reduced sample in the Fe^{2+} - Fe^{3+} coexisting state is focused. Because of the charge neutrality and the attractive interaction, Fe^{2+} is associated with an oxygen vacancy ($\text{V}_{\text{O}}^{\bullet\bullet}$). Half of Fe^{3+} also forms an Fe^{3+} - $\text{V}_{\text{O}}^{\bullet\bullet}$ associate and the other half is isolated. The defect (gap) states are schematized for the **a** Fe^{2+} - $\text{V}_{\text{O}}^{\bullet\bullet}$ and **b** Fe^{3+} - $\text{V}_{\text{O}}^{\bullet\bullet}$ cells. The k -weighted and averaged energy differences are indicated by black arrows. The right and left states are the majority ($\uparrow$) and minority ($\downarrow$) spin components, respectively, and electrons occupying in the gap states are denoted by red and blue arrows in their corresponding spin bands. The partial charge densities near Fe atoms at the Γ point are displayed: the Fe^{2+} - $\text{V}_{\text{O}}^{\bullet\bullet}$ cell has the **b** d_{z^2} ($\downarrow$) and **c** $d_{x^2-y^2}$ ($\uparrow$) states, while the Fe^{3+} - $\text{V}_{\text{O}}^{\bullet\bullet}$ cell involves the **e** d_{xz} - d_{yz} ($\downarrow$) (degenerate), **f** d_{z^2} ($\downarrow$), and **g** d_{xy} ($\downarrow$) states. The partial charge densities in the $\uparrow$ and $\downarrow$ bands are coloured light blue and yellow, respectively. The Fe^{2+} - $\text{V}_{\text{O}}^{\bullet\bullet}$ cell shows the electron-occupied $d_{x^2-y^2}$ ($\uparrow$) state at a depth of 2.3 eV from the CBM and the occupied d_{z^2} ($\downarrow$) state at 1.5 eV from the CBM. The Fe^{3+} - $\text{V}_{\text{O}}^{\bullet\bullet}$ cell contains the empty d ($\downarrow$) states at 1.8 to 1.9 eV from the VBM. Reprinted from Noguchi Y. *Nat. Commun.* 2020;11(1): 1–10. Copyright 2020 Nature Publishing Group.

In the Fe^{3+} cell (Figs. 14a and 14b), the empty t_{2g} ($\downarrow$) state arises in the bandgap at a depth of 1.9 to 2.3 eV from the valence band maximum (VBM). For the Fe^{3+} - $\text{V}_{\text{O}}^{\bullet\bullet}$ cell (Figs. 14c and 14d), four empty bonding ($\downarrow$) states appear near the middle of the bandgap; at the Γ point, two are low-lying degenerate states of Fe - $3d_{xz}$ and $-3d_{yz}$ (Fig. 15e), and the remaining two are higher-lying Fe - $3d_{z^2}$ (Fig. 15f) and $-3d_{xy}$ (Fig. 15g) states. The energy difference between these gap states and the VBM is 1.8 to 2.1 eV. Both for the single isolated Fe^{3+} and the Fe^{3+} - $\text{V}_{\text{O}}^{\bullet\bullet}$ associate (Fig. 15d), it is considered that visible light at $h\nu$ above 1.8 to 1.9 eV pumps electrons from the VBM to the empty states, namely, visible light drives $h^\bullet$ injection from Fe^{3+} to the valence band. This is accomplished by an electron transfer to Fe^{3+} from the adjacent atoms, which is associated with a reduction from Fe^{3+} to Fe^{2+} .

Figures 14e and 14f displays the electronic structure of the Fe^{2+} - $\text{V}_{\text{O}}^{\bullet\bullet}$ cell, and a schematic representation is shown in Fig. 15a. There exists several Fe - $3d$ derived states in the bandgap: the low-lying two states are elec-

tron filled, whereas three states near the conduction band minimum (CBM) are empty. The filled Fe - $3d_{z^2}$ ($\downarrow$) state (Fig. 15b) arises in the middle of the bandgap, which is positioned at a depth of 1.5 to 1.9 eV from the CBM. Therefore, this occupied state is capable of delivering an onset of electron injection to the conduction band at this photon energy. As shown in Fig. 15c, the occupied Fe - $3d_{x^2-y^2}$ ($\downarrow$) state exists. Because this state is positioned at a depth of 2.3 to 2.6 eV from the CBM, an additional onset of electron injection arises at ≈ 2.3 eV. These electron pumping can be regarded as an electron transfer from Fe^{2+} to titanium, which is accompanied by an oxidation from Fe^{2+} to Fe^{3+} .

In the Fe^{2+} and Fe^{3+} coexisting state under illumination, the first onset is at ≈ 1.5 eV, above which the electron in the Fe^{2+} - $3d_{z^2}$ ($\downarrow$) state is pumped to the conduction band (Fig. 15a). This provides a PV response that arises from electron conduction through a trapping-detraping process.^{160),161),188)} The second onset is at 1.8 to 1.9 eV, above which holes are injected into the valence band from the empty gap states ($\downarrow$) of Fe^{3+} (Fig. 15d). At $h\nu$ greater than the second onset energy, the photoinduced carrier is e' - $h^\bullet$ pair. The third onset is at 2.3 eV, above which the electron in the Fe^{2+} - $3d_{x^2-y^2}$ ($\uparrow$) state is additionally injected into the conduction band (Fig. 15a). Above the third onset, e' - $h^\bullet$ pairs are effectively created, because visible light can pump electrons from the valence band to the conduction band mediated through these occupied and empty gap states. Electrons are excited from the two occupied states of Fe^{2+} ($\rightarrow \text{Fe}^{3+}$), and holes are injected into the valence band from the empty gap states of Fe^{3+} ($\rightarrow \text{Fe}^{2+}$). This sequential electron pumping is accompanied by two successive redox reactions of $\text{Fe}^{3+}/\text{Fe}^{2+}$.

4.5 PV properties

Figure 16 shows the current density divided by optical intensity, $J_{\text{sc}} I_{\text{opt}}^{-1}$, with respect to $h\nu$. The samples exhibit a complicated PV response above E_g of 3.2 eV. Here, the PV properties at $h\nu$ below E_g is focused.

The oxidized (Figs. 16a and 16b) and non-doped samples exhibit a PV onset at 1.9 to 2.0 eV, which corresponds the energy difference between the VBM and the empty states of the isolated Fe^{3+} and the Fe^{3+} - $\text{V}_{\text{O}}^{\bullet\bullet}$ associate (Fig. 14). In Figs. 16c and 16d, the reduced sample exhibits a large $J_{\text{sc}} I_{\text{opt}}^{-1}$ in a wide $h\nu$ range. It is postulated that the first onset is below 1.6 eV, which is in good agreement with the 1.5 eV difference of the CBM to Fe^{2+} - $3d_{z^2}$ ($\downarrow$) (Fig. 15a). The second onset is at ≈ 1.9 eV, which corresponds to the difference between the VBM and the empty Fe^{3+} ($\downarrow$) states (Fig. 15b). The third onset is at ≈ 2.4 eV, which is the gap of the CBM to the filled Fe^{2+} - $3d_{x^2-y^2}$ ($\uparrow$) state. These light induced current onsets are in good agreement with the results of photoluminescence measurements.²⁹⁾

5. Future prospects

For the development of MLCCs with Ni electrodes,^{116),117),189)–197)} not only acceptors (Mn, Cr, Ca,

Fig. 16. PV currents versus photon energy.²⁹⁾ The short-circuit current density (J_{sc}) normalized by optical intensity (I_{opt}) is plotted as a function of photon energy ($h\nu$) for the **a, b** oxidized and **c, d** reduced samples. The valence state of iron in the oxidized sample is Fe^{3+} as the majority, while that in the reduced sample is a mixture of Fe^{2+} and Fe^{3+} . The first PV onset is determined as the threshold by considering the noise level and the strong emissions of Xe lamp (light source) in the near-infrared range. The oxidized sample displays the first PV onset at 1.9 to 2.0 eV. The reduced sample exhibits a multiple-PV process: the first PV onset appears at less than 1.6 eV followed by the second at 1.9 eV and the third at 2.4 eV. Reprinted from Noguchi Y. *Nat. Commun.* 2020;11(1):1–10. Copyright 2020 Nature Publishing Group.

and Mg etc.)^{25),26),116),117),190),191),198)} but also RE elements^{199)–201)} such as Dy and Ho etc. play a crucial role for dielectric and reliability properties and for long lifetime. Because Ni is apt to be oxidized during heating, the ceramics with Ni electrodes have to be sintered at a relatively low pO_2 . This heating process is accompanied more or less by oxygen vacancies and thereby often induces a transition from a p-type insulating (oxidized) to n-type semi-conducting (reduced) state when a sufficient acceptor is not included. Therefore, so-called non-reducible ceramics have been developed by a codoping of the acceptors along with the RE elements; the details are described in the review paper by Kishi et al.⁴⁾

While the roles of the acceptors are well understood, those of the RE elements remain still elusive,^{202)–210)} even though there is no doubt about their importance. Establishing the defect chemistry including the role of RE elements is a major challenge to be overcome, where the combination of the defect thermodynamics described above and DFT calculations provides a possible clue.

It is also expected that the defect control will provide materials design for photocatalysts. As a representative, TiO_2 ²¹¹⁾ absorbs only ultraviolet light owing to its large bandgap (E_g), several approaches for controlling the electronic structure have been employed to induce a visible-light response: creating donor levels into the bandgap via doping,^{212),213)} lifting the valence band to a more negative level than that arising from O-2p,^{214),215)} and narrowing the bandgap.^{216),217)}

For $SrTiO_3$, Reunchan et al.²¹⁸⁾ report that the Fermi-level lifting by a co-doping promotes a photocatalytic

response under visible light, which is achieved by stabilizing Cr^{3+} in the presence of La^{3+} . Defect levels inside the bandgap, called gap states, of Cr^{3+} are located above the VBM, and the donor states play a crucial role in visible-light activation.²¹⁹⁾ Wang et al.²²⁰⁾ show that La- and Rh-codoped $SrTiO_3$ functions as a photocatalyst, where the occupied states of Rh^{3+} narrows the bandgap.

The methodology for the visible light activation utilizing two redox states²⁹⁾ can be applied for the photocatalysts. In these titanate systems, rigid TiO_6 octahedra govern the electronic structure near the bandgap, and the overall features of the iron-derived gap states are essentially identical. Furthermore, the multivalent cations are not the unique dopants for $e'-h^*$ pair generation. A codoping can be employed: donor and acceptor states arise from cations of different elements, in which their defect concentrations are controllable. The strategy employing the donor and acceptor states offers a starting point for further investigation of successive redox-mediated functions and opens an unprecedented route to robust photoinduced effects based on gap-state engineering.

Acknowledgements This research is partly supported by JSPS through Grant-in-Aid for JSPS Fellows (26-4693). This research is partly supported by JSPS KAKENHI Grant Numbers 26249094 and 17H06239. The author would like to thank Prof. Miyayama and all the members in our laboratory as well as my collaborators for their advice and support to conduct my research work.

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