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

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,¹⁰⁻¹² 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 1980s,²⁰⁻²³ 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 composed 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, sounded 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
2. Defect chemistry

2.1 Kröger-Vink notation

From the past to the present, the nomenclature proposed by Kröger and Vink, so called, the Kröger-Vink notation 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 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.

![Figure 2](image)

Kröger-Vink notation explicitly expressing defect species in crystalline solids.

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: V₉⁰ with doubly positive charges, V₉ with singly positive charge, and V₉⁻ with charge neutral. At extremely LTs, V₉ that captures two electrons around it is assumed to exist, whereas the presence has never been reported as a majority. For BaTiO₃, V₉⁻ has proven to be the major vacancy in the wide temperature range even at room temperature, indicating that the concentration of V₉₀ [V₉⁻] is orders of magnitude lower than that of V₉⁻ [V₉⁻⁻]. For SrTiO₃, V₉⁻ plays an important role in defect-related properties at LTs. It is indicated that V₉⁻ is the majority at room temperature, the situation of [V₉⁻⁻] > [V₉⁻] occurs below 550 °C and is maintained down to extremely LTs. Other papers report that [V₉⁻⁻] is still much lower than [V₉⁻⁻] at above room temperature. Saraf et al. clearly show that the acceptor (Fe) doped SrTiO₃ in the p-type region have a high [V₉⁻⁻] (10¹⁶–10¹⁸/cm³) by over five orders of magnitude compared with [V₉⁻⁻] (below ~10¹³/cm³) while the donor (Nb) doped one in the n-type region displays extremely low concentrations (below ~10⁹/cm³) of [V₉⁻⁻] and [V₉⁻⁻], 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 (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 Tc 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) and on the Ti site (Ca⁺Ti) as is described later.

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

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| Table 1: Representative Defects in BaTiO₃ |
|-------------------------------------------|
| Element or Vacancy | Site | Charge |
| Ba²⁺ | Ba | Neutral |
| Ti⁴⁺ | Ti | Neutral |
| O²⁻ | O | Neutral |
| V₉₀ | Bath | Doubly Negative |
| V₉⁻⁻ | Bath | Doubly Positive |
| V₉⁻⁻ | Bath | Triply Negative |
| V₉⁻⁻ | Bath | Triply Positive |
| V₉⁻⁻ | Bath | Neutral |

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Ti⁴⁺ site, and the charge imbalance is compensated by a formation of oxygen vacancy (V₉⁰). Cations on the interstitial sites are possible species, but these interstitial defects are negligible in perovskite oxides. 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.

Moreover, an interaction between impurity ions and V₉⁰ is being understood. 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, 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 (PZT), Pb(Mg₁/₃Nb₂/₃)O₃ (PMN), and PbTiO₃ (PT).

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On the Ti site, wide variation of transition metal cations play a role of acceptor; one of the cations providing a
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 limit is as small as several percent124) or up to 20%125) and the solubility limit in Bi4Ti3O12 is up to several percent.124) The solubility limit is as small as several percent.124) The solubility is reported to be 5%126) or up to 20%127) and the solubility limit in Bi4Ti3O12 is up to several percent.126)

The concentration of A remains constant regardless of a heating or cooling, as assumed in the literature,114,129) the total concentration of A is unchanged (m_A is dosage of A):

\[
    m_A = [\text{A}^{III}] + [\text{A}^{II}] + [\text{ATi}^+].
\]

The charge neutrality condition is expressed as

\[
    2[\text{ATi}^{III}] + [\text{ATi}^+] + n = 2[V_O] + p,
\]

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

\[
    \text{null} \leftrightarrow e' + h*.
\]

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

\[
    K_i(T) = n \cdot p = N_C(T) \cdot N_V(T) \exp[\frac{-[E_g(0 K) - \beta T]}{kT}],
\]

where N_C(T) and N_V(T) are the effective densities of states in the conduction band and the valence band, respectively,27) and k the Boltzmann constant, E_g (0 K) the band gap at 0 K, and \( \beta \) its temperature coefficient.110) The formation of V_O in Bi4Ti3O12 is written as

\[
    O_2^- \leftrightarrow V_O + 1/2 O_2 (g) + 2e',
\]

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

\[
    K_{red} = \frac{[V_O]^{2/2}}{n^2} = \frac{K_C^{\text{red}}}{\exp(-\Delta H_{\text{red}}/kT)}.
\]

The ionization reactions of A on the Ti^{4+} site can be described by the generations either of e' or h*, while these are exactly identical.22,23,117,118,133) Here, the expressions based on the h* generation are adopted. By producing h*, A ions can be ionized negatively, and the ionizations of A ions are expressed as

\[
    \text{A}^{III} \leftrightarrow \text{A}^{II} + h*, \quad (K_{h1}, \Delta H_{h1}),
\]

\[
    \text{A}^{II} \leftrightarrow \text{A}^{I} + h*, \quad (K_{h2}, \Delta H_{h2}),
\]

where their respective equilibrium constants (K_{h1} and K_{h2}) and enthalpies (\( \Delta H_{h1} \) and \( \Delta H_{h2} \)) hold

\[
    K_{h1} = p[\text{A}^{II}]/[\text{A}^{III}] = K_{h1}^{\text{eq}} \exp(-\Delta H_{h1}/kT),
\]

\[
    K_{h2} = p[\text{Fe}^{III}]/[\text{Fe}^{II}^{\text{eq}}] = K_{h2}^{\text{eq}} \exp(-\Delta H_{h2}/kT),
\]

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

### 2.5 Relation among the enthalpies through E_g

The formula 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

| Table 1. Representative intrinsic point defects, acceptors, donors, and neutral defects in BaTiO_3. RE denotes RE elements (La, Nd, Sm, Dy, Ho, etc.) and TM indicates 3d-transition metal elements |
|------------------------------|-----------------|-------------------|
| Site         | Acceptor | Neutral | Donor |
| Ba^{2+}      | \( V_{\text{Ba}}^{\text{III}} \) (vacancy) | \( \text{Ca}^{2+} \), \( \text{Sr}^{2+} \), \( \text{RE}^{3+} \) (RE = RE elements) | \( \text{Bi}^{3+} \), \( \text{Bi}^{4+} \), \( \text{Bi}^{5+} \) |
| Ti^{4+}      | \( V_{\text{Ti}}^{\text{III}} \) (vacancy) | \( \text{Mg}^{2+} \), \( \text{Ca}^{2+} \), \( \text{Sr}^{2+} \), \( \text{Sn}^{2+} \), \( \text{TM}^{3+} \) (TM = 3d-transition metal) | \( \text{Ga}^{3+} \), \( \text{Zn}^{2+} \), \( \text{Mn}^{2+} \), \( \text{Fe}^{3+} \), \( \text{Fe}^{2+} \), \( \text{Al}^{3+} \), \( \text{Co}^{2+} \) |
| \( \text{O}^{2-} \) | \( N_{\text{O}}^{\text{III}} \) (N^{3-}) | \( F^{-} \) (F^-) | \( \text{V}^{\text{V}}^{2+} \) |

\* 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% (Ba_{0.87}Ca_{0.13})TiO_3.122) The solubility limit is as small as several percent124) or up to 20%125) and the solubility limit in Bi_{4}Ti_{3}O_{12} is up to several percent.126) The solubility limit cannot be read in the paper126) and the solubility limit in Bi_{4}Ti_{3}O_{12} is up to several percent.126) The solubility limit is as small as several percent124) or up to 20%127) and the solubility limit in Bi_{4}Ti_{3}O_{12} is up to several percent.126) The solubility limit is as small as several percent124) or up to 20%127) and the solubility limit in Bi_{4}Ti_{3}O_{12} is up to several percent.126)
are connected through $E_h$. 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 $A_{Ti}^N / A_{Ti}^{N-1}$ and $A_{Ti}^{N+1} / A_{Ti}^{N}$ 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 $A^N$ and $A'$ are given as

$$A^N \leftrightarrow A^0 + e' (K_{a1}, \Delta H_{a1}),$$

$$A' \leftrightarrow A^0 + e' (K_{a2}, \Delta H_{a2}),$$

where $K_{a1}$ and $K_{a2}$ denote their respective equilibrium constants, and $\Delta H_{a1}$ and $\Delta H_{a2}$ are 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:

$$\Delta H_{a1} + \Delta H_{b1} = E_g,$$

$$\Delta H_{a2} + \Delta H_{b2} = E_g.$$  

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

$$2A^N + 1/O_2 + V_{O}^{**} \leftrightarrow 2A' + O_2,$$

$$K_{ox1} = [A^N]^2[V_{O}^{**}]^2[O_2]^{-1},$$

$$= K_{ox1} \exp(\Delta H_{ox1}/kT).$$

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

$$2A' + 1/O_2 + V_{O}^{**} \leftrightarrow 2A^N + O_2,$$

$$K_{ox2} = [A'^N]^2[V_{O}^{**}]^2[O_2]^{-1},$$

$$= K_{ox2} \exp(-\Delta H_{ox2}/kT),$$

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

$$2E_g = \Delta H_{red} + \Delta H_{ox1}.$$  

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

$$2E_g = \Delta H_{red} + \Delta H_{ox2} (\Delta H_{ox1} = \Delta H_{ox2}).$$  

Note that the $\Delta H_{ox1}$ and $\Delta H_{ox2}$ 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; $[V_{O}^{**}]$ 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 spcies of $V_{O}^{**}, A'$ (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 are minor. In the higher $pO_2$ regime, the p-type conduction prevails with its conductivity $\sigma_p \propto p \propto pO_2^{3/4}$, where the charge neutrality condition is $[A'] \approx 2[V_{O}^{**}]$. In the lower $pO_2$ regime, the n-type conduction is dominant with its conductivity $\sigma_n \propto n \propto pO_2^{-3/4} ([A'] \approx 2[V_{O}^{**}]$) at the intermediate $pO_2$ and $n \propto pO_2^{-3/4}$ at the extremely low $pO_2$. It is worth noting that the data near the conductivity minimum are approximately higher than the extrapolated lines of $\sigma_p \propto pO_2^{3/4}$ and $\sigma_n \propto pO_2^{-3/4}$. 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 \([V^\text{Ti}_\text{vac}]\) 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 \((V^\text{Ti}_\text{vac}, A', e' and h')\) govern the conductivity behavior and also that the mobilities of \(e'\) and \(h'\), 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.\(^{28},29,113,140,144,146\) the total oxygen vacancy concentration in the HT equilibrium states \([V^\text{O}_\text{vac}] + [V^\text{O}_\text{vac}]\) 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 is 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 \([V^\text{O}_\text{vac}] + [V^\text{O}_\text{vac}]\) 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-doped SrTiO\(_3\) 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, \(P_{O_2}\).\(^{113}\) Defect concentration labels without HT and LT indices remain virtually unchanged during quenching. Mass action constants are taken from the collection in the paper\(^{41}\) except that a concentration of 0.8 at% of an acceptor with an ionization energy \(\Delta H_{A1} = 1\text{ eV}\) was assumed for the calculation: \((- - -)\) electron and hole concentrations, \((\cdot \cdot \cdot)\) oxygen vacancy concentration, \((\cdot \cdot \cdot)\) doubly ionized acceptor, \((-\cdot\cdot\cdot)\) 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.

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

Waser also reported the schematic conductivity diagram for acceptor (Ni)-doped SrTiO\(_3\) in the LT quenched state after equilibration.\(^{113}\) With decreasing \(pO_2\), the majority carrier changes from \(h^+\), \(O^{2-}\) (\(V^\text{O}_\text{vac}\)), to \(e'\), and thereby the dominant conduction mechanism also changes from hole conduction (total conductivity \(\sigma_{tot} \approx \sigma_{h^+}\)), oxide-ion conduction (\(\sigma_{tot} \approx \sigma_{V^\text{O}_\text{vac}} = \sigma_{O^{2-}}\)) to electron conduction (\(\sigma_{tot} \approx \sigma_{e'}\)). As explained above, the redox couple \(A'/A''\) (\(Ni^{3+}/Ni^{2+}\)) acts as a trap for \(h^+\), and its conductivity is relatively low with the relation of \(\sigma_{h^+} \propto P_{O_2}^{-1/4}\). In the intermediate \(pO_2\) regime, \(\sigma_{V^\text{O}_\text{vac}}\) prevails and does not depend on \(pO_2\), because \([V^\text{O}_\text{vac}]\) remains constant (\(\Delta n^+ \approx [V^\text{O}_\text{vac}]\)). At low \(pO_2\), \(\sigma_{e'}\) is dominant and its value is up to four orders of magnitude higher than \(\sigma_{h^+}\). 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 \(pO_2\); next, under the fixed value of \([V^\text{O}_\text{vac}]\) at each \(pO_2\), all the other concentrations in the LT quenched state are calculated as a function of \(T\).

#### 3.1 Ba(Ti,Ca)O\(_3\)

As described above, \(Ca^{3+}\) can be positioned both on the Ba site (\(Ca_{Ba}^{3+}\))\(^{115}\) and on the Ti site (\(Ca_{Ti}^{3+}\))\(^{116,117}\) which depends on the boundary condition such as the
composition. Here, the role of Ca as an acceptor, $Ca^{2+}_{Ti}^{\prime}$, 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 reported to be 0.54 eV in the temperature range of 827–977 °C.\(^{(48)}\)

$$Ca^{2+}_{Ti}^{\prime} \leftrightarrow Ca^{2+}_{Ti}^{\prime\prime} + h^{\star}, \quad (\Delta H_h), \quad (21)$$

It should be emphasized that $Ca^{2+}_{Ti}^{\prime}$ is regarded not as $Ca^{2+}$ but as $Ca^{2+}$ as a defect complex of $Ca^{2+}$ 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 $\beta = 3.7 \times 10^{-4} \text{eV K}^{-1}$.\(^{(48)}\)

**Figure 6** shows the defect concentration diagram of $Ba(Ti_{1-x}Ca)_2O_3$ ($x = 0.005$) 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 $Ca^{2+}_{Ti}^{\prime}$ ($[Ca^{2+}_{Ti}^{\prime}] \approx [V_{O}^{\ast\ast}]$ except at an extremely low $pO_2$); $[Ca^{2+}_{Ti}^{\prime\prime}]$ is orders of magnitude higher than $[Ca^{2+}_{Ti}^{\prime}]$. With decreasing $pO_2$ from 1 atm, $V_{O}^{\ast\ast}$ is indeed generated, where the charge neutrality is satisfied by a decrease in $[Ca^{2+}_{Ti}^{\prime}]$, see Eq. (7). In this regime, the electronic carrier is $h^{\star}$ (p-type) which is detrapped in a thermally activated process with $\Delta H_h$. A carrier crossover appears at $pO_2 \sim 10^{-8} \text{ atm}$, where $e^{\prime}$ prevails over $h^{\star}$; the electronic conduction changes from p-type to n-type, delivering a V-shaped conductivity.\(^{(117)}\) With further decreasing $pO_2$, the charge balance is maintained by Eq. (5). At below $pO_2 < 10^{-6} \text{ atm}$, the charge neutrality condition is approximated as $n \approx 2[V_{O}^{\ast\ast}]$ with $n \propto pO_2^{-1/6}$.\(^{(9)}\)

**Figure 7** shows the defect concentration diagram of $Ba(Ti_{1-x}Ca)_2O_3$ ($x = 0.005$) at 25 °C after equilibration at 900 °C along with an electronic conduction behavior. The $[V_{O}^{\ast\ast}]$ values equilibrated at 900 °C is assumed to be frozen-in and thereby the horizontal axis denotes $pO_2$ at 900 °C.

![Defect concentration diagram for Ba(Ti_{1-x}Ca)_2O_3 (x = 0.005) at 25 °C after equilibration at 900 °C along with an electronic conduction behavior.](image)

**Figure 6.** Defect concentration diagram for Ba(Ti_{1-x}Ca)_2O_3 ($x = 0.005$) in an equilibrium state at 900 °C. The horizontal axis is the $pO_2$ at 900 °C and the vertical axis is the defect concentrations in the linear scale (a), (b) and in the logarithmic scale (c).

**Figure 7.** Defect concentration diagram for Ba(Ti_{1-x}Ca)_2O_3 ($x = 0.005$) at 25 °C after equilibration at 900 °C along with an electronic conduction behavior. The $[V_{O}^{\ast\ast}]$ values equilibrated at 900 °C is assumed to be frozen-in and thereby the horizontal axis denotes $pO_2$ at 900 °C.

**3.2 Ba(Ti,Mn)O_3**

The valence state of Mn on the Ti site varies among $Mn^{2+}$ ($Mn^{2+}_{Ti}^{\prime}$), $Mn^{3+}$ ($Mn^{3+}_{Ti}^{\prime}$), and $Mn^{4+}$ ($Mn^{4+}_{Ti}^{\prime}$).\(^{(4,25,26,129,136,149,150)}\) Hagemann and Hennings have reported the hole generation enthalpy $\Delta H_h (1.87 \text{ eV})$ associated with the redox reaction of $Mn^{3+}_{Ti}^{\prime}$/$Mn^{3+}_{Ti}^{\prime}$ and the $\Delta H_h (1.28 \text{ eV})$ with that of $Mn^{3+}_{Ti}^{\prime}$/$Mn^{3+}_{Ti}^{\prime\prime}$ in the temperature range of 800–1,200 °C. The $\Delta H_h (0 \text{K})$ of 2.30 eV and the $\Delta H_h (0 \text{K})$ of 1.71 eV are adopted along with $\beta = 3.7 \times 10^{-4} \text{eV K}^{-1}$, corresponding to $\Delta H_h (900 \text{ °C}) = 1.87 \text{ eV}$ and $\Delta H_h (900 \text{ °C}) = 1.23 \text{ eV}$.

**Figure 8** shows the defect concentration diagram of $Ba(Ti_{1-x}Mn)_2O_3$ ($x = 0.001$) in an HT (900 °C) equilibrium state. Note that with decreasing $pO_2$ from 1 atm the majority of Mn ion changes from $Mn^{2+}$ to $Mn^{4+}$. In the higher $pO_2$ region at above $10^{-5} \text{ atm}$, the charge neutrality condition is expressed as $[Mn^{3+}_{Ti}^{\prime}] \approx 2[V_{O}^{\ast\ast}]$. An increase in $pO_2$ oxidizes $Mn^{3+}_{Ti}^{\prime}$ to $Mn^{4+}_{Ti}^{\prime}$ and thereby $[V_{O}^{\ast\ast}]$ is reduced. In the intermediate $pO_2$ region of $10^{-15}$–$10^{-5} \text{ atm}$, the charge neutrality condition is $2[Mn^{3+}_{Ti}^{\prime}] + [Mn^{3+}_{Ti}^{\prime\prime}] \approx 2[V_{O}^{\ast\ast}]$. With decreasing $pO_2$ further, the charge neutrality condition changes from $n + 2[Mn^{3+}_{Ti}^{\prime}] + [Mn^{3+}_{Ti}^{\prime\prime}] \approx 2[V_{O}^{\ast\ast}]$ ($10^{-22}$–$10^{-15} \text{ atm}$) to $n \approx 2[V_{O}^{\ast\ast}]$ ($pO_2 < 10^{-22} \text{ atm}$). 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 $Mn^{3+}_{Ti}^{\prime}/Mn^{3+}_{Ti}^{\prime}$ and $Mn^{3+}_{Ti}^{\prime}/Mn^{3+}_{Ti}^{\prime\prime}$ play a role, as indicated in Eqs. (9) and (10).

**Figure 9** shows the defect concentration diagram of $Ba(Ti_{1-x}Mn)_2O_3$ ($x = 0.001$) in the LT (25 °C) quenched...
state. With decreasing $pO_2$, there exists two distinct thresholds: one is $pO_2^{\text{p-p}}$ at which a carrier crossover between p-type and n-type occurs, and the other is $pO_2^{\text{n-n}}$ at which a transition from an n-type insulation to an n-type semiconductor. Even though the Mn content is as low as 0.1%, the $pO_2$ with an insulating feature is extended down to $10^{-17}$ atm.

At $pO_2 > pO_2^{\text{p-p}}$, the $\text{Mn}^{4+}/\text{Mn}^{4+}$ couple acts as a trap for $h^+$ 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 $pO_2$ ($pO_2^{\text{n-n}}>pO_2>pO_2^{\text{p-p}}$) the redox reaction owing to $\text{Mn}^{4+}/\text{Mn}^{4+}$ can trap $e^-$ and thereby the n-type insulation is seen; the $n$ is below $10^2$ cm$^{-2}$, which is orders of magnitude lower than that in Ca-doped BaTiO$_3$ (see Fig. 7). At below $pO_2^{\text{n-n}}$, the $n$ is extremely high, leading to an n-type semiconductor, as displayed in Fig. 7.

Figure 10 shows the evolution of the defect concentration diagram of Ba(Ti$_{1-x}$Mn$_x$)O$_3$ ($x = 0.001$) in the LT (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 $[V_{\text{O}^*}^\circ]$ decrease because of the negative $\Delta H_{\text{Ox1}}$ and $\Delta H_{\text{Ox2}}$; II. the $\text{Mn}^{4+}$ and $\text{Mn}^{3+}$ majority regions are widened; III. the $pO_2^{\text{p-p}}$ and $pO_2^{\text{n-n}}$ thresholds decrease monotonically, i.e., the insulation region is spread down to $pO_2 \approx 10^{-26}$ atm at $T^{eq} = 700$ °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 $[V_{\text{O}^*}^\circ]$ 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 (La, Sr)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.151-153) 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$^{2+}$-derived acceptor state act as robust scaffolds for generating e$^-$$h^+$ pairs under visible light.29)

4.1 Bulk PV effect

The polar lattice with spatial inversion symmetry breaking arises in the bulk PV effect$^{13,(150,157)}$ associated with
high voltages beyond the bandgap limit of semiconductor p-n junctions.\textsuperscript{156-159} The ferroelectric PV effect appears under ultraviolet light for wide-bandgap oxides such as LiNbO\textsubscript{3},\textsuperscript{156,159,160} BaTiO\textsubscript{3},\textsuperscript{11,12,162} and BiFeO\textsubscript{3}.\textsuperscript{158,159,165} The poor absorption of visible light is improved by band-gap narrowing,\textsuperscript{166-170} which is accompanied by a substantial decrease in $P_e$. Gap-state engineering employing mid-gap states for BiFeO\textsubscript{3} 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 BaTiO\textsubscript{3} (3.2 to 3.3 eV),\textsuperscript{172,173} the PV effect arises under ultraviolet light. To activate a visible-light response, electronic states derived from Fe\textsuperscript{2+} and Fe\textsuperscript{3+} are introduced into the bandgap, and these gap states are utilized as scaffolds for carrier generation.

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

Figure 11e shows the defect concentration diagram at 25°C as a function of $pO_2=900$ torr in Fe (0.3 %)-doped BaTiO\textsubscript{3} where four regions exist. In the regions I and II, the majority of iron is trivalent, namely, [Fe\textsuperscript{3+}]; Fe\textsuperscript{3+} is orders of magnitude higher than others; the minority is Fe\textsuperscript{4+} at a higher $pO_2$ (I) and Fe\textsuperscript{2+} at a lower $pO_2$ (II). The region III is the coexisting state of Fe\textsuperscript{3+} and Fe\textsuperscript{2+}; the concentrations of which have the same order. At the higher $pO_2=900$ torr (III and II), the charge neutrality is $2[FeTi\textsuperscript{3+}]+[FeTi\textsuperscript{2+}]=2[V_{O_{1}}\textsuperscript{*}]$. The region IV is semiconducting with a high $n$, along with Fe\textsuperscript{2+} as the majority ($n \approx 2[VO\textsuperscript{*}]$). It is expected that the region III is capable of providing a robust PV response under visible light. Therefore, an $pO_2=900$ torr of 10\textsuperscript{-3} atm is adopted as an annealing condition, where the concentrations are calculated to be $[FeTi\textsuperscript{2+}] \approx 3.5 \times 10^{19}$ cm\textsuperscript{-3} and $[FeTi\textsuperscript{2+}] \approx 4.3 \times 10^{19}$ cm\textsuperscript{-3}.

4.3 Defect associates

Figure 12 shows the density-functional theory (DFT) energy with $n$ of $V_{O_{1}}\textsuperscript{*}$, where $VO\textsuperscript{*}$ denotes the $V_{O_{1}}\textsuperscript{*}$ 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 $VO\textsuperscript{*}$. Because $VO\textsuperscript{*}$ has a certain mobility even below the $T_C$, $VO\textsuperscript{*}$ is trapped by Fe and is eventually positioned on the nearest-neighbour (NN) O1 site (Figs. 13b and 13e) after a
certain period. In aged samples, $V_{0}^{\ast}$ exists as a defect associate of Fe$^{3+}$-$V_{0}^{\ast}$ and/or Fe$^{2+}$-$V_{0}^{\ast}$.

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 ($\uparrow$) and minority ($\downarrow$) spin bands. In the $\uparrow$ 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 Fe$^{3+}$-$V_{0}^{\ast}$ and Fe$^{3+}$-$V_{04}^{\ast}$ 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 Fe$^{3+}$-$V_{01}^{\ast}$ cell are lower in energy by $\approx0.5$ eV than those of the Fe$^{3+}$-$V_{01}^{\ast}$ cell. The attractive interaction between Fe$^{3+}$ and $V_{0}^{\ast}$ originates from these low-lying bonding states. As for Fe$^{2+}$, the Fe$^{2+}$-$V_{01}^{\ast}$ cell has electron-filled gap states: the Fe-3$d_{x^2}$ state ($\uparrow$) and the Fe-3$d_{z^2}$ state ($\downarrow$). The remaining $t_{2g}$ states, namely, Fe-3$d_{x^2}$, Fe-3$d_{y^2}$, Fe-3$d_{xy}$, and Fe-3$d_{yz}$, are located at lower energy and are near the valence band bottom. The stabilization of $V_{0}^{\ast}$ on the O1 site, i.e., the formation of the Fe$^{2+}$-$V_{01}^{\ast}$ associate, arises from these lower-lying Fe-3$d$ states.

Because a short-range $V_{0}^{\ast}$ motion with a distance of a few unit cells occurs even near room temperature,\textsuperscript{147,180} it is reasonable to assume that all oxygen vacancies are present as the defect associates of Fe$^{3+}$-$V_{0}^{\ast}$ and/or Fe$^{2+}$-$V_{0}^{\ast}$ in the samples, as reported for SrTiO$_3$.\textsuperscript{181,182} and PbTiO$_3$.\textsuperscript{183,184} and BaTiO$_3$.\textsuperscript{185,186}

### 4.4 Gap states of Fe-3d

Figure 14 shows the electronic structures of the Fe$^{3+}$-$V_{0}^{\ast}$, and Fe$^{2+}$-$V_{0}^{\ast}$ cells (their crystal structures in Fig. 13). In Fig. 15, the defect levels for the Fe$^{3+}$-$V_{01}^{\ast}$ and Fe$^{2+}$-$V_{01}^{\ast}$ cells are schematized, where the corresponding wavefunctions of the Fe-3d derived gaps states are displayed. As reported in the literature,\textsuperscript{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.
the other half is isolated. The defect (gap) states are schematized for photoresponse of the reduced sample in the Fe$^{2+}$-occupied densities in the respective. The Fe$^{2+}$dx$^2$-O1$^\text{**}$ state arises in the bandgap at a depth of 1.9 to 2.3 eV from the CBM, an additional onset of electron injection arises at $\approx$2.3 eV. These electron pumping can be regarded as an electron transfer from Fe$^{2+}$ to Fe$^{3+}$.

In the Fe$^{2+}$ and Fe$^{3+}$ coexisting state under illumination, the first onset is at $\approx$1.5 eV, above which the electron in the Fe$^{2+}$-3d$^2$ (↑) state is pumped to the conduction band (Fig. 15a). This provides a PV response that arises from electron conduction through a trapping-detrapping process. 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 (↓) of Fe$^{3+}$ (Fig. 15d). At hv greater than the second onset energy, the photoinduced carrier is e$^-$-h$^*$ pair. The third onset is at 2.3 eV, above which the electron in the Fe$^{2+}$-3d$^3$ (↑) state is additionally injected into the conduction band (Fig. 15a). Above the third onset, e$^-$-h$^*$ 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$^{2+}$ (→Fe$^{3+}$), and holes are injected into the valence band from the empty gap states of Fe$^{3+}$ (→Fe$^{2+}$). This sequential electron pumping is accompanied by two successive redox reactions of Fe$^{3+}$/Fe$^{2+}$.

4.5 PV properties

Figure 16 shows the current density divided by optical intensity, $J_{sc}$/$I^{opt}$, with respect to hv. The samples exhibit a complicated PV response above $E_0$ of 3.2 eV. Here, the PV properties at hv below $E_0$ 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 to the energy difference of the VBM and the empty states of the isolated Fe$^{3+}$ and the Fe$^{3+}$-V$\text{O}_{12}^{\text{**}}$ associate (Fig. 14). In Figs. 16c and 16d, the reduced sample exhibits a large $J_{sc}$/$I^{opt}$ in a wide hv 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$^2$ (↑) (Fig. 15a). The second onset is at $\approx$1.9 eV, which corresponds to the difference between the VBM and the empty Fe$^{3+}$ (↑) states (Fig. 15b). The third onset is at $\approx$2.4 eV, which is the gap of the CBM to the filled Fe$^{2+}$-3d$^3$ (↑) state. These light induced current onsets are in good agreement with the results of photoluminescence measurements.

5. Future prospects

For the development of MLCCs with Ni electrodes, not only acceptors (Mn, Cr, Ca, tron filled, whereas three states near the conduction band minimum (CBM) are empty. The filled Fe$^{3+}$-3d$^1$ (↑) 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$^{3+}$-3d$^3$ (↑) 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 $\approx$2.3 eV. These electron pumping can be regarded as an electron transfer from Fe$^{2+}$ to Fe$^{3+}$.

In the Fe$^{2+}$ and Fe$^{3+}$ coexisting state under illumination, the first onset is at $\approx$1.5 eV, above which the electron in the Fe$^{2+}$-3d$^2$ (↑) state is pumped to the conduction band (Fig. 15a). This provides a PV response that arises from electron conduction through a trapping-detrapping process. 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 (↓) of Fe$^{3+}$ (Fig. 15d). At hv greater than the second onset energy, the photoinduced carrier is e$^-$-h$^*$ pair. The third onset is at 2.3 eV, above which the electron in the Fe$^{2+}$-3d$^3$ (↑) state is additionally injected into the conduction band (Fig. 15a). Above the third onset, e$^-$-h$^*$ 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$^{2+}$ (→Fe$^{3+}$), and holes are injected into the valence band from the empty gap states of Fe$^{3+}$ (→Fe$^{2+}$). This sequential electron pumping is accompanied by two successive redox reactions of Fe$^{3+}$/Fe$^{2+}$.
and Mg etc.\textsuperscript{(25,26,116,117,190,191,198)} but also RE elements\textsuperscript{(199)} 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\textsubscript{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 semiconducting (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.\textsuperscript{(4)}

While the roles of the acceptors are well understood, those of the RE elements remain still elusive.\textsuperscript{(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\textsubscript{2}\textsuperscript{211)} absorbs only ultraviolet light owing to its large bandgap (E\textsubscript{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\textsuperscript{(212,213)} lifting the valence band to a more negative level than that arising from O-2p\textsuperscript{(214,215)} and narrowing the bandgap.\textsuperscript{(16,217)}

For SrTiO\textsubscript{3}, Reunchan et al.\textsuperscript{(218)} report that the Fermi-level lifting by a co-doping promotes a photocatalytic response under visible light, which is achieved by stabilizing Cr\textsuperscript{3+} in the presence of La\textsuperscript{3+}. Defect levels inside the bandgap, called gap states, of Cr\textsuperscript{3+} are located above the VBM, and the donor states play a crucial role in visible-light activation.\textsuperscript{(219)} Wang et al.\textsuperscript{(220)} show that La- and Rh-codoped SrTiO\textsubscript{3} functions as a photocatalyst, where the occupied states of Rh\textsuperscript{3+} narrows the bandgap.

The methodology for the visible light activation utilizing two redox states\textsuperscript{(29)} can be applied for the photocatalysts. In these titanate systems, rigid TiO\textsubscript{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\textsuperscript{-}h\textsuperscript{+} 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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