Theoretical and experimental investigation of defect formation / migration in Gd$_2$Ti$_2$O$_7$: General rule of oxide-ion migration in A$_2$B$_2$O$_7$ pyrochlore

Kaoru Nakamura, Masashi Mori, Takanori. Itoh, and Toshiharu Ohnuma

Central Research Institute of Electric Power Industry, 2-6-1 Nagasaka, Yokosuka, Kanagawa 240-0196, Japan
Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan

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We investigated the intrinsic defect formation energy and oxide-ion migration mechanism in Gd$_2$Ti$_2$O$_7$ pyrochlore. It was found that the vacancy formation energy of Gd is lower than that of Ti. For the oxygen vacancy, O(48f) was found to show lower vacancy formation energy than O(8b). The formation energy of the vacancy complex showed that the Gd vacancy is accompanied with the O(48f) vacancy, which is consistent with our experiment. The migration energy of O(48f) along the <100> direction, which is dominant migration path for ionic conduction, was calculated to be 0.43 eV. On the other hand, we found that Gd vacancy increases O(48f) migration energy. For example, the migration energy of O(48f) along the <100> direction was increased to be 1.36 eV by the local compressive strain around Gd vacancy. This finding could explain our previous experimental result of decreasing conductivity with increasing Gd deficiency. Along with the oxide-ion migration mechanism in Gd$_2$Ti$_2$O$_7$, O(48f) migration energies along both <100> and <110> directions for various A$_2$B$_2$O$_7$ pyrochlore structures were investigated. As a general trend of oxide-ion migration in the pyrochlore structure, we propose that O(48f) migration along the <100> direction is governed by the strength of B–O bonding. On the other hand, the ratio of ionic radius B/A is proposed to determine O(48f) migration along the <110> direction in A$_2$B$_2$O$_7$ pyrochlore. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4967211]

I. INTRODUCTION

In addition to ABO$_3$ perovskite, A$_2$B$_2$O$_7$ pyrochlore is also a multifunctional material featuring ferroelectricity, radiation damage resistance, high ionic conductivity, superconductivity, and geometrically frustrated magnetism. These wide varieties of physical properties are due to its complicated atomic configurations and resultant electronic structures. The pyrochlore structure is closely related with the BO$_2$ fluorite structure. In the fluorite structure (space group Fm$ar{3}$m, no. 225), the cation forms an fcc configuration (4a: (0,0,0)), and oxygen occupies eight interstitial sites (8c: (0.25,0.25,0.25)). On the other hand, the pyrochlore structure (space group Fd$ar{3}$m, no. 227) is frequently called the “vacancy ordered fluorite structure”, in which two different cation elements are orderly positioned along the <110> direction. Different cation ordering splits the 4a site within the fluorite structure into 16d: (0.5, 0.5, 0.5) and 16c: (0, 0, 0) sites in the pyrochlore structure. Accordingly, oxygen sites also split into 48f: (x, 0.125, 0.125) and 8b: (0.375, 0.375, 0.375) sites (x is the 48f parameter) because of the different bonding characteristics of A–O and B–O. In addition, an oxygen-vacant 8a site is also introduced within all $B_4$ tetrahedrons to preserve charge neutrality.

Corresponding author. n-kaoru@criepi.denken.or.jp. Tel: +81 46 856 2121. Fax: +81 46 856 5571

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These structural features seem to be especially favorable to achieve high ionic conductivity because oxide-ion can easily migrate from one site to the unoccupied equivalent site. However, the experimentally measured oxygen ionic conductivity of pyrochlores is not very high compared with the representative fluorite, Yttria-Stabilized Zirconia (YSZ). In YSZ, additional extrinsic oxygen vacancy is introduced by Y₂O₃ doping. Along with this conductivity enhancement of YSZ, the effect of A-site deficiency on the crystal structure, sintering property, thermal expansion and electrical conductivity of Gd₂₋₇Ti₇O₁₅₋₈ pyrochlores was investigated by one of the present authors. Contrary to the expectation, it was found that the electrical conductivity decreased with increasing A-site deficiency, whereas sinterability increased. The underlying mechanism of the decrease in electrical conductivity has remained unclear, and should be instructive to control the electrical conductivity of pyrochlores.

The ionic conductivity is governed by the fast ionic diffusion, whereas sintering and grain growth are controlled by the slowest diffusing species. Thus, it is crucial to investigate the defect formation and migration to understand the microscopic mechanism of ionic conductivity and sintering kinetics. Defect formation and migration energies of Gd₂Ti₂O₇ were previously investigated by static lattice calculation using parameterized inter-atomic potentials by Wilde and Catlow. They showed that the vacancy hopping mechanism between 48f sites is dominant in the ionic conductivity of pyrochlores. Pirzada et al. also investigated the general rule of oxide-ion migration in A₂B₇O₁₅ pyrochlore including Gd₂Ti₂O₇, using the same methodology. However, oxide-ion migration in Gd₂Ti₂O₇ has not been investigated at the electronic level. In addition, because defect formation in oxide materials is strongly dependent on the preparing condition, the theoretical defect formation energy must be calculated under various equilibrium conditions by first-principles calculation. Although Wang et al. and Xiao et al. investigated the defect formation energy of Gd₂Ti₂O₇ using first-principles calculation, they did not consider vacancy but rather cation anti-sites and oxygen Frenkel pairs. This situation seems to have partly originated in the fact that pyrochlores have been widely investigated in terms of radiation damage, because they are applied to ceramic waste forms for actinide immobilization.

Therefore, in this study, we systematically investigated defect formation and oxide-ion migration in Gd₂Ti₂O₇ as a model pyrochlore structure from the perspective of the electronic nature. Further discussion will be provided on the relationship between the present theoretical results and the experimental measurements, in order to understand the origin of the conductivity decrease in Gd₂₋₇Ti₇O₁₅₋₈ pyrochlores as the A-site deficiency. Moreover, by extending the obtained results for Gd₂Ti₂O₇, a general rule for ionic migration in A₂B₇O₁₅ pyrochlore will be re-investigated from the viewpoint of the chemical bonding and ionic radii, to show deeper insights for pioneering works.  

II. EXPERIMENTAL AND CALCULATION METHOD

A. First-principles calculation

First-principles calculations were performed with the Vienna Ab-initio Simulation Package (VASP). Interactions between ions and electrons were described by the Projected Augmented Wave (PAW) method. Perdew–Burke–Ernzerhof revised for solids (PBEsol) was utilized to approximate exchanges and correlate interactions of electrons. PBEsol was proposed to suppress the well-known overestimation of the lattice constants in Generalized Gradient Approximation (GGA). Gd 4f electron was basically assumed to be fully shielded by the 5d⁰ and 6s² valence electrons and treated as a frozen core state. To verify this assumption, the case of Gd 4f electrons as valence was also checked. When Gd 4f electrons were included in the valence state, spin polarization was also considered. Although the ground state of the magnetic structure in Gd₂Ti₂O₇ is the anti-ferromagnetic spin configuration of Gd ions, it orders below 1.0 K. In addition, our calculation showed that the energy difference between ferromagnetic and anti-ferromagnetic spin configuration was approximately 1 meV/atom, which does not affect our results and conclusion. Therefore, we assumed a ferromagnetic spin configuration in the case of including the Gd 4f electrons as valence.

The kinetic cut-off energy for the plane wave was 500 eV. The k-point mesh for integration in the Brillouin zone was carefully selected as a Γ-point centered 4 × 4 × 4 k-mesh for a Gd₂Ti₂O₇ primitive cell. These calculation conditions were confirmed to be sufficient to acquire well-converged
total energy, below 0.1 meV/atom. Defect formation energies and migration energies were evaluated in $2 \times 2 \times 2$ expanded supercells (176 atoms) based on a primitive cell (22 atoms). Only the $\Gamma$-point was used for the expanded supercell because of the computational efficiency. It was confirmed that denser $2 \times 2 \times 2$ $k$-mesh ensures energy convergence for the supercell below 4 meV/atom, which does not change our results and conclusions. Atomic positions and cell parameters were optimized until the forces on each atom and cell converged below $5 \times 10^{-4}$ eV/Å.

Within the supercell, we removed or added one ion to introduce the isolated vacancy or interstitial defect. All defects were assumed to be neutral and ionized up to their formal charges. Isolated defect formation energy $E_f$ was calculated by the following equation:

$$ E_f = E_T(\text{defect}; q) - \{E_T(\text{perfect}) - \Sigma n_i \mu_i\} + q(\varepsilon_F + E_{\text{VBM}}) \quad (1) $$

where $E_T(\text{defect}; q)$ and $E_T(\text{perfect})$ are total energies of the defect-containing supercell and a perfect one, respectively. $q$ is the charge state of the defect. To preserve the charge neutrality within the supercells, additional jellium background charges were introduced. In eq. (1), $n_i$ and $\mu_i$ are the number and chemical potential of defect species $i$, respectively. $\varepsilon_F$ is the fermi energy, and $E_{\text{VBM}}$ is the energy of the valence band maximum. $E_{\text{VBM}}$ was determined by the following equation:

$$ E_{\text{VBM}} = E_{\text{VBM(perfect)}} + V_{\text{av(defect)}} - V_{\text{av(perfect)}} \quad (2) $$

$$ E_{\text{VBM(perfect)}} = E_{\text{T(perfect:0)}} - E_{\text{T(perfect: +1)}} \quad (3) $$

where $V_{\text{av}}$ is the averaged electrostatic potential. When the defect is introduced, $V_{\text{av(defect)}}$ can be evaluated by averaging electrostatic potentials at the farthest sites from the defect. $E_{\text{T(perfect:0)}}$ and $E_{\text{T(perfect: +1)}}$ are the total energies of the perfect cell of the neutral charge state and that when one electron is removed, respectively. With eq. (1), Fermi energy $\varepsilon_F$ was assumed to be a relative value measured from $E_{\text{VBM}}$ because the vacuum level cannot be determined in the usual calculation of density functional theory. The detailed calculation method of point defect formation energy is well summarized in the literature and applied for various oxide materials.

Figure 1 shows the schematic illustration of the Gd–Ti–O pseudo ternary phase diagram. Because the chemical potential $\mu_i$ of element $i$ ($i = \text{Gd, Ti, O}$) is dependent on the equilibrium condition, the following equilibrium conditions were considered at each equilibrium point shown in Fig. 1:

A: $2\mu_{\text{Gd}} + 3\mu_{\text{O}} = \mu_{\text{Gd}_2\text{O}_3(\text{bulk})}$, $\mu_{\text{O}} = \mu_{\text{O(gas)}}$
B: $\mu_{\text{Ti}} + 2\mu_{\text{O}} = \mu_{\text{TiO}_2(\text{bulk})}$, $\mu_{\text{O}} = \mu_{\text{O(gas)}}$
C: $\mu_{\text{Ti}} + 2\mu_{\text{O}} = \mu_{\text{TiO}_2(\text{bulk})}$, $2\mu_{\text{Ti}} + 3\mu_{\text{O}} = \mu_{\text{Ti}_2\text{O}_3}$
D: $2\mu_{\text{Ti}} + 3\mu_{\text{O}} = \mu_{\text{Ti}_2\text{O}_3}$, $\mu_{\text{Ti}} + \mu_{\text{O}} = \mu_{\text{TiO}(\text{bulk})}$
E: $\mu_{\text{Ti}} + \mu_{\text{O}} = \mu_{\text{TiO}(\text{bulk})}$, $\mu_{\text{Ti}} = \mu_{\text{TiO}(\text{bulk})}$
F: $\mu_{\text{Ti}} = \mu_{\text{Ti}(\text{bulk})}$, $\mu_{\text{Gd}} = \mu_{\text{Gd}(\text{bulk})}$
G: $\mu_{\text{Gd}} = \mu_{\text{Gd}(\text{bulk})}$, $2\mu_{\text{Gd}} + 3\mu_{\text{O}} = \mu_{\text{Gd}_2\text{O}_3(\text{bulk})}$

FIG. 1. Schematic illustration of the Gd–Ti–O pseudo ternary phase diagram. Equilibrium conditions of each point (point A to G) are explained in the text.
where $2\mu_{\text{Gd}} + 2\mu_{\text{Ti}} + 7\mu_{\text{O}} = \mu_{\text{Gd}_2\text{Ti}_2\text{O}_7(\text{bulk})}$ was assumed to be always preserved. It is well known that Local Density Approximation (LDA) or GGA underestimates the bandgap. This could be the source of error in the defect formation energy if an additional defect level is formed near the bottom of the conduction band. In such a case, the defect formation energy was corrected by adding the value of $m \cdot \Delta E_g$, where $m$ is the number of electrons occupied at the defect level,$^{16,17}$ $\Delta E_g$ was obtained by the difference between the theoretical bandgap (calculated by PBEsol+ $U$ functional with explicitly considered Gd 4f electrons as valence) and the one calculated by PBEsol functional. It should be mentioned that the calculated band gap by hybrid HSE06 functional$^{31}$ was 4.41 eV, which is far from experimental band gap values. For the PBEsol+ $U$ functional with Dudarev’s approach,$^{32}$ effective $U$ ($U_{\text{eff}} = U - J$) values of Gd 4f electrons and Ti 3d electrons were determined to reproduce the experimentally determined bond lengths and lattice constant of Gd$_2$Ti$_2$O$_7$. The resultant effective $U$ value was determined to be 5 eV for Gd 4f electrons and 4 eV for Ti 3d electrons. Although these $U_{\text{eff}}$ values are different from the literature,$^{33}$ they determined $U_{\text{eff}}$ (6.9 eV for Gd 4f electrons) from the fitting of Gd$_2$O$_3$.($^{33}$)

Because the bonding strength is also an essential factor to determine the ionic migration, the following chemical bonding analysis was performed. The net charge of the ion was calculated by Bader analysis,$^{34}$ which assigns electrons to a specific ion by a partitioning method enclosed with inflection points of the spatial charge distribution. Ionic bonding strength was evaluated by the form of the electrostatic attractive force using net charges. For the covalent bonding, the bond overlap population was calculated by the integration of crystal orbital overlap population (COOP) analysis utilizing Local-Orbital Basis Suite Towards Electronic-Structure Reconstruction (LOBSTER) code$^{35–37}$ after structural relaxation by VASP code.$^{22}$ The basis sets used were 6s$^2$5p$^5$5d$^4$4f$^7$ for Gd, 4s$^2$3p$^6$3d$^2$ for Ti and 2s$^2$2p$^4$ for oxygen. Because chemical bonding analysis is largely basis dependent, additional calculations were performed using Mulliken population analysis by the atomic orbital approach of Siesta code with a minimal basis$^{38}$ to verify the obtained bond overlap population.

The ionic migration was investigated by the Climbing Image Nudged Elastic Band (CINEB) method.$^{39}$ The vacancy mechanism (including intrinsic vacant site, 8a) was assumed to be the migration path. The migration energy was calculated as the energy difference between the initial state and the saddle point state. To eliminate artificial interactions between neighboring cells, the migration energy was calculated using a 2 $\times$ 2 $\times$ 2 expanded supercell, which ensures that the distance between vacancies of adjusting cells is longer than 10 Å. The $\Gamma$-point was used for integration in the Brillouin zone. A number of CINEB images were selected whose distance between images was approximately 1 Å.

B. Experimental procedure

The gadolinium titanate powders were synthesized by a solid-state reaction technique. The starting material powders, Gd$_2$O$_3$ (preheated at 1773 K for 1 h) (99.9%, High Purity Chem., Japan) and TiO$_2$ (preheated at 1637 K for 1 h) (99.9%, rutile phase, High Purity Chem., Japan), were used. They were weighed and mixed in a rotary-type Y$_2$O$_3$ partially stabilized ZrO$_2$ ball mill for 24 h with isopropyl alcohol. The mixtures were heated to 1473 K in air after drying and held at this temperature for 6 h. The powders were uniaxially pressed into a tablet under a pressure of 98 MPa, and the tablets were isostatically pressed at a pressure of 200 MPa. The tablets were then sintered at 1813–1833 K for 12 h in air, at a heating/cooling rate of 6 K/min. The milling and heating procedures were repeated twice.

The crystal structures of Gd$_2$Ti$_2$O$_7$ series were determined by Rietveld refinements by using the synchrotron X-ray diffraction (SR-XRD) data. SR-XRD experiments were carried out using a large Debye–Scherrer camera installed in a BL19B2 beamline with the bending magnet in SPring-8 under proposal no. 2007B1915 (Hyogo, Japan). The SR-XRD data were measured in the 2$\theta$ range of 5–70° with a wavelength of 0.50047 Å, which was determined by calibrating a National Institute of Standards and Technology (NIST) CeO$_2$ standard sample for a step interval of 0.01°.

Diffraction data of Gd$_2$Ti$_2$O$_7$ series with the space groups $Fd\bar{3}$ $m$ were analyzed by the Rietveld refinement technique using the computer program RIETAN-FP,$^{40}$ and the Maximum Entropy Method (MEM) was carried out using the PRIMA program.$^{41}$ The SR-XRD measurements were refined using the modified split pseudo-Voigt function proposed by Izumi and Ikeda.$^{42}$ The crystal structures and
charge densities of the samples were visualized by using the software package VESTA.\textsuperscript{43} MEM was carried out on a unit cell of Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} series, which was distributed across 128 \times 128 \times 128 pixels.

III. RESULTS AND DISCUSSIONS

A. Structure and electronic properties of Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}

The optimized crystal structure of Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} is shown in Fig. 2, in which cubic representation is used instead of the primitive cell. The cubic unit cell is shown as the solid square. Gray lines are first nearest neighboring (1st NN) bonds between cations (Gd–Gd, Ti–Ti and Gd–Ti). Two oxygen sites, O(48f) and O(8b), are represented by red and yellow balls, respectively. Purple balls are Gd ions of the 16d position, and blue balls are Ti ions of the 16c position. To understand the complicated pyrochlore structure, vacant 8a sites are also shown in Fig. 2 with gray balls. The characteristic structural parameters (lattice constant, 48f parameter and bond length), which were calculated by different exchange-correlation functionals, are summarized in Table I. Except for the bond length of Gd–O(48f), calculation errors are within 1\% of the experimental value, which is common error in first-principles calculation. The values of $R_{wp}$, $S$ and $R_B$ fitting parameters obtained at Rietveld refinement are equal to 9.82, 3.10 and 3.42, respectively and seem to be satisfactory.

The calculated net charges (Bader charge minus number of valence electrons of the pseudo potential) of each element and bond overlap population are summarized in Table II. By the presence of the shared electron and charge transfer from Gd ion or Ti ion to oxide-ion, the net charges of ions are different from their formal charges. It is found that O(48f) attracts more electrons than O(8b), and Ti ion shows more deviation from the formal charge than Gd ion. Thus, both Gd–O and Ti–O have mixed characteristics of ionic and covalent bonding. For the strength of ionic bonding, Gd–O(8b) is found to be stronger than Gd–O(48f) because of the longer bond length of Gd–O(48f). These characteristics were not changed by the functional selection. Although chemical bonding analysis is well known to be dependent on the basis set, the obtained results of covalent bonding strength could well explain the vacancy formation energies and ionic migration energies of Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}. Therefore, values of the integrated COOP will be used as bond overlap populations (BOP) to discuss the covalent chemical bonding strength in this study. Whereas the calculated BOP among Gd–O(48f), Gd–O(8b) and Ti–O(48f) show different values dependent on the functional selection, it was confirmed to be common that Gd–O(8b) shows the weakest covalent character. The BOP of Gd–O was found to be mainly composed of Gd 5d–O 2p interaction, where the 4f orbital did not participate as much in the chemical bonding. Different BOPs between Gd–O(8b) and Gd–O(48f) are thought to stem from

![FIG. 2. Schematic illustration of the crystal structure of Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}. Cubic unit cell is represented as the solid square. For clarity, not only irreducible atomic sites (Gd(16d), Ti(16c), O(48f) and O(8b)) but also the vacant 8a site is explicitly shown. Gray lines represent first-nearest neighboring bonds between cations.](image-url)
the different bond lengths. For Ti–O(48f), the BOP was composed of Ti 3d and O 2p interaction. Here, the covalent binding strength of each ion can be evaluated by the summation of BOPs of all neighboring bonds. The resultant covalent binding strength around O(48f) was 0.326, whereas that around O(8b) was 0.348. Thus, it can be said that O(8b) is more covalently bound than O(48f) in the Gd$_2$Ti$_2$O$_7$ lattice, which is consistent with the oxygen vacancy formation energy.

Figures 3 (a) and (b) show the total and partial densities of states (PDOS) for Gd$_2$Ti$_2$O$_7$ using (a) PBEsol and (b) PBEsol+$U$ functionals. Zero energy was set at the valence band maximum. In the PDOS of Figs. 3, the orbital-decomposed DOSs are colored black for s-orbital, red for p-orbital, blue for d-orbital and green for f-orbital. Note that the Gd pseudopotential with frozen 4f electrons was used for PBEsol calculation, whereas the other functional used an explicitly treated 4f state as valence. As in Ref. 34 Gd 4f states are seen to participate in chemical bonding more or less because it spread over ∼5 eV below the Fermi level (e$_F$) and overlapped with 2p states of O(8b) and O(48f). Experimentally determined values of the bandgap of Gd$_2$Ti$_2$O$_7$ are reported to be 3.0 eV$^{44}$ and 2.82 eV$^{45}$, which are quite close to the calculated bandgap ∼3.01 eV of the present PBEsol+$U$ result. On the other hand, the bandgap of Gd$_2$Ti$_2$O$_7$ single crystal is reported to be 1.5 eV by the activation energy of electrical conductivity from 675 K to 1000 K.$^{46}$ However, that value does not necessarily correspond to the bandgap because ionic conduction is overlooked.

Overlapping between Gd 4f and O 2p electrons is apparently seen in the charge density distributions. Fig. 4 (a) shows the partial valence charge density calculated by the PBEsol+$U$ functional within the energy range of -5 eV to 0 eV (measured from the Fermi energy). Electrons are localized at Gd–O(8b) and Ti–O(48f) bonds, and the covalent character can be easily seen. When the Gd 4f state was considered as the frozen core state (corresponding to Fig. 3(a)), the charge localization at Gd–O(8b) bond was less significant within the aforementioned energy range. Fig. 4 (b) shows the experimental charge density obtained by maximum entropy method (MEM) analysis. The minimum charge density between Ti ion and O(48f) was 0.78 e/Å$^3$, whereas it was 0.64 e/Å$^3$ between Gd ion and O(8b). However, the BOP of Gd–O(8b) was comparable to that of Ti–O(48f), as shown in Table II.
FIG. 3. Density of states of each element in Gd$_2$Ti$_2$O$_7$ calculated by (a) PBEsol with frozen-core Gd 4f electrons and (b) PBEsol+U with Gd 4f electrons. Fermi energies were set to be zero energy, shown as vertical lines. For partial density of states, orbital decomposed contributions are represented as black (s), red (p), blue (d) and green (f) lines.

Although both Gd 4f and O 2p electrons are distributed at the same energy level, chemical bonding analysis revealed that the BOP was mainly composed of Gd 5d–O 2p hybridization. Actually, it was confirmed that considering Gd 4f electrons did not crucially affect the calculated defect formation.

FIG. 4. (a) Decomposed valence charge density within the energy level of -5 eV to 0 eV. Energy was measured from Fermi energy. (b) Experimental total charge density obtained by MEM analysis. Isosurfaces were shown at (a) 0.02 e/Å$^3$ and (b) 0.70 e/Å$^3$. Gd–O and Ti–O bonds are represented as gray lines in Fig. 4(a) to show the different chemical bonding structures.
FIG. 5. Neutral defect formation energies of (a) interstitial defects and (b) vacancies at each equilibrium point shown in Fig. 1. Frenkel-type defect formation energies of O(48f) and O(8b) are shown as solid lines. The dotted line shows the formation energy of the cation anti-site.

energies and the ionic migration energies. Thus, the results calculated by using the PBEsol functional are basically shown in the following section.

B. Defect formation in Gd$_2$Ti$_2$O$_7$

The calculated neutral defect formation energies of the interstitial site and vacancy at each equilibrium condition (shown in Fig. 1) are shown in Figs. 5 (a) and (b), respectively. The difference in the calculated defect formation energies between PBEsol and PBEsol+$U$ functional was no more than 0.3 eV, whose error does not change the following discussion. The lower significance of the Gd 4f electrons was also shown in the high-pressure phase transformation of Gd$_2$Ti$_2$O$_7$ and Gd$_2$Zr$_2$O$_7$.\textsuperscript{47} The left sides of Figs. 5 (a) and (b) correspond to the oxidation limit (e.g., points A and B), whereas the right sides of Figs. 5 (a) and (b) correspond to the reduction limit (e.g., points F and G). It is clear that the formation energies of the interstitial site and vacancy show an inverse relationship. Under the oxidation limit at points A and B in Fig. 5 (a), the oxygen interstitial at the vacant 8a site shows the lowest formation energy. Moreover, the oxygen vacancies show lower formation energy than those of cation vacancies under the reduction limit at points C to G in Fig. 5 (b). For the cation interstitial, both Gd and Ti interstitials show almost comparable formation energies. In the pyrochlore structure, the octahedral site, enclosed by three A and B ions (Gd$_3$Ti$_3$), can be considered as the interstitial site, rather than the 8a site. It was found that the Gd interstitial is more stable at the octahedral site than at the vacant 8a site, independent of the charged state. At the octahedral site, the formation energy differences of neutral Gd, Ti and O interstitials from those at the 8a site are -1.28 eV, +0.08 eV and +0.79 eV, respectively. Because the ionic radius of Gd is larger than that of Ti\textsuperscript{48} and the cage size of Gd$_3$Ti$_3$ (octahedral site) is larger than Ti$_4$ (8a site), it is thought that Gd ion is more comfortable at the octahedral site than at the 8a site. Actually, the distance between the interstitial Gd at the 8a site and surrounding four Ti ions is 2.647 Å, whereas that distance of Ti ion at the 8a site is 2.473 Å. For the oxygen interstitial at the octahedral site, its position was relaxed towards the Ti ion side rather than the Gd ion side within the Gd$_3$Ti$_3$ cage. In contrast, the interstitial oxygen at the 8a site (O(8a)) was stable at the center of the Ti$_4$ cage. Qualitatively, oxide-ion tends to form a covalent bond with Ti ion rather than Gd ion. Therefore, it can be considered that the different number of Ti ion and interstitial oxygen bonds affects the stability of the O(8a) and that at the octahedral site. Figures 5 shows formation energies of the oxygen Frenkel pair and the cation antisite as solid and dotted lines, respectively. The oxygen Frenkel pair was considered by displacing the O(48f) or O(8b) into their first nearest neighbor 8a site. The Frenkel pair of O(8a)–V$_{O(48f)}$ (represented as O(48f) => 8a in Figs. 5) is found to show the lower formation energy than that of O(8a)–V$_{O(8b)}$ independent of the equilibrium condition.

Figure 5 (b) shows that the vacancy formation energy of O(48f) is lower than that of O(8b) by 2.23 eV. This result is consistent with that of the chemical bonding analysis, in which O(48f) is more
weakly bonded than O(8b) in Gd$_2$Ti$_2$O$_7$. For the cation vacancy, the formation energy of the Gd vacancy is lower than that of the Ti vacancy at every equilibrium condition. This indicates that the Gd deficiency can be more easily introduced than the Ti deficiency under the oxidation condition. Here, this vacancy is usually charged, and its formation energy is dependent on the chemical potential of the electron—i.e., Fermi energy.

Figure 6 shows the vacancy formation energies as a function of the Fermi energy at each equilibrium point, as shown in Fig. 1. The Fermi energy was varied from zero to the theoretical bandgap calculated by using the PBEsol+$U$, 3.01 eV. Gradients of each line correspond to the charged states of the vacancies. As with the neutral vacancy, the formation energy of O(48f) is always lower than that of O(8b), independent of the Fermi energy. Moreover, the Ti vacancy shows lower formation energy than the Gd vacancy when the Fermi energy is located near the bottom of the conduction band, especially under the oxidation limit (at equilibrium points of A). In our experiment, Gd vacancy was introduced as A-site deficiency. In this case, the Fermi level is thought to be located near the top of the valence band, where O(48f) vacancy shows the lowest formation energy. Therefore, it can be considered that O(48f) vacancy also introduces coupling with Gd vacancy even at the oxidation condition. If oxygen vacancies are introduced at first under the reduction condition, cation vacancy formation energies can be reduced because the oxygen vacancy shifts the Fermi level near the bottom of the conduction band. These tendencies are related to the well-known self-compensation of defect complex.\(^{17}\)

To consider the interactions between charged defects, the formation energies of Gd vacancy and oxygen vacancy complex were calculated as shown in Fig. 7. Black lines with filled symbols in Fig. 7 show the formation energies of explicitly considered defect complexes of the Gd vacancy and its first nearest neighbor oxygen vacancy. An energetically favorable configuration of Gd vacancy and oxygen vacancy was confirmed to be mutual first nearest neighboring position. It is easily found that $V_{\text{Gd}}-V_{O(48f)}$ is more stable than $V_{\text{Gd}}-V_{O(8b)}$ at every equilibrium condition shown in Fig. 1. This order

![Figure 6](image-url)

**FIG. 6.** Vacancy formation energies as a function of the Fermi energy at each equilibrium point shown in Fig. 1. Fermi energy was measured from the top of the valence band and varied from zero to the calculated bandgap of the PBEsol+$U$, 3.01 eV. Gradients of each line indicate the charged states of vacancies.
is the same as the formation energy of the isolated oxygen vacancy of \( V_{\text{O}(48f)} \) and \( V_{\text{O}(8b)} \). Colored lines with open symbols show the Schottky-type defect formation energies of \( 2V_{\text{Gd}}^{3+} + 3V_{\text{O}(48f)}^{2+} \) and \( V_{\text{Ti}}^{-4} + 2V_{\text{O}(48f)}^{2+} \), in which each formation energy of the isolated charged vacancy was summed up. Except for the reduction limit at the F point in Fig. 1, \( 2V_{\text{Gd}}^{3+} + 3V_{\text{O}(48f)}^{2+} \) is more stable than \( V_{\text{Ti}}^{-4} + 2V_{\text{O}(48f)}^{2+} \).

These calculated results of defect formation energies are consistent with our present experiment. Fig. 8 shows the oxygen occupancy determined by SR-XRD measurement and subsequent Rietveld analysis. As the Gd deficiency increased, the occupancy of \( \text{O}(48f) \) decreased while that of \( \text{O}(8b) \) was constant. After the annealing under \( \text{H}_2 \) atmosphere, the occupancy of \( \text{O}(48f) \) further decreased, which indicates that the number of the \( \text{O}(48f) \) vacancies increased. This increase in \( \text{O}(48f) \) vacancies corresponds to the change in the equilibrium condition. As shown in Fig. 5 (b), the oxygen vacancy formation energy in the reduction condition is lower than that in the oxidation condition. Thus, the Gd vacancy formation and the \( \text{O}(48f) \) vacancy formation have an indispensable relation with each other.

C. Oxide-ion migration in \( \text{Gd}_2\text{Ti}_2\text{O}_7 \)

1. \( \text{O}(48f) \) migration in perfect crystal

Figures 9 (a) to (c) show the migration paths of \( \text{O}(48f) \). The calculated migration energies of \( \text{O}(48f) \) are summarized in Table III. It was confirmed that the order of the migration energies of each path is independent of the choice of the functional and consideration of the Gd 4f electrons.
Fig. 9(a) shows the oxide-ion migration from O(48f) to V_{O(48f)} nearly along the <100> direction. The obtained migration energy of O(48f) along <100> was 0.43 eV, which is not necessarily low for the high ionic conductor. However, oxide-ion migration energy from O(48f) to the second nearest neighboring (2nd NN) V_{O(48f)} along the <110> direction, shown in Fig. 9(b), was calculated to be 0.1 eV and much lower than that from O(48f) to the 1st NN V_{O(48f)} (O(48f) migration along <100> direction). However, O(48f) migration along <100> direction is dominant for the ionic conduction in pyrochlore as indicated by early investigation,\textsuperscript{14} because O(48f) cannot diffuse the whole lattice by only along <110> direction. These characteristic migration mechanisms were actually confirmed to occur by additional first-principles molecular dynamics simulations.

The trajectories of the O(48f) migrations are illustrated in Figs. 10 (a) and (b) as successive gray balls, in which the configuration of cations at the saddle point is represented. Because of the crystal structure of pyrochlore, the oxide-ion draws close to the surrounding cation during migration. This is thought to be the origin of the energy barrier of the oxide-ion migration. In the migration path of O(48f) along the <100> direction, oxide-ion must pass between Gd and Ti ions, positioned along <110>. At the saddle point, shown in Fig. 10 (a), the distance between Gd and Ti ions was 3.992 Å, whereas it was originally 3.577 Å in the perfect Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} lattice. The bond lengths of Gd–O and Ti–O at the saddle point in Fig. 10 (a) were 2.200 Å and 1.792 Å, respectively, which are approximately 10% shorter compared with the pristine bond lengths. In contrast, the migrating O(48f) does not get as close to the surrounding cations in the migration path of O(48f) along the <110> direction. At the saddle point, the migrating O(48f) is close to two Ti ions, and their bond lengths are 1.873 Å and 1.907 Å. Thus, in the case of O(48f) migration along the <110> direction, the local strain around the migrating oxide-ion is lower than the case of O(48f) migration along <100>. This point must be responsible for the low migration energy of O(48f) along <110>. Moreover, the

| Migration specie | Migration path | Corresponding Fig. | Migration energy (eV) |
|------------------|----------------|--------------------|----------------------|
| O(48f)           | V_{O(48f)} <100> | Fig. 9(a)          | 0.43 (1.36)          |
| O(48f)           | V_{O(48f)} <110> | Fig. 9(b)          | 0.05 (0.20)          |
| O(48f)           | 8a              | Fig. 9(c)          | 0.66                 |
oxide-ion migrations shown in Figs. 10 (a) and (b) can be represented as the rotation of the Ti–O bonding. Therefore, migration energies of O(48f) are thought to include the strain energy of bending of the Ti–O bond.

It should be noted here that the O(48f) migration along \( \langle 110 \rangle \) is identical to the successive oxide-ion migration from the 48f site to the 2nd NN 48f site via the vacant 8a site. The migration path of the oxide-ion along the \( \langle 100 \rangle \) direction from the 48f site to the vacant 8a site is illustrated in Fig. 9 (c). Migration of O(48f) to the vacant 8a site corresponds to the formation of the oxygen Frenkel-type defect. Because the migration energy of O(48f)–8a (almost comparable with the Frenkel-type defect formation energy, shown as a red solid line in Figs. 5) is larger than that of the O(48f), it can be considered that oxide-ion migrates to avoid the energetically unfavorable state, O(8a) site in Gd\(_2\)Ti\(_2\)O\(_7\).

2. O(48f) migration around Gd vacancy

As shown above, the O(48f) migration energy of Gd\(_2\)Ti\(_2\)O\(_7\) pyrochlore is significantly affected by the local atomic configuration. This idea can be applied to understand the effect of Gd vacancy on oxide-ion migration. Localized structural relaxations around the vacancies are summarized in Table IV as the changes in the distance between the introduced vacancies and nearest neighboring ions. The distance between ions was considered up to 4 Å. Around the Gd vacancy, both Ti ion and O(48f) show outward relaxation from the vacancy, whereas Gd ion and O(8b) show the inward relaxation. With regard to the Ti vacancy, both Gd and Ti ions approach the Ti vacancy, whereas O(48f) moves away from the Ti vacancy. Moreover, the cation moves away from the oxygen vacancies when oxide-ion approaches. This structural relaxation behavior around the vacancies can be basically understood by the coulomb interaction between charged vacancies and surrounding ions. Positively charged cations approach the negatively charged cation vacancies, whereas negatively charged oxide-ion moves away, and vice versa. An exception can be found in \( V_{\text{Gd}}^{-3} - \text{O}^{-2} \) and \( V_{\text{Gd}}^{-3} - \text{Ti}^{4+} \). Because Gd–O(8b) has a more covalent character than Gd–O(48f), as discussed in the previous section, the repulsive coulomb interaction should be lower for Gd–O(8b) compared with Gd–O(48f). Actually, O(48f) largely moves away from the Gd vacancy. Thus, because Ti ion is bonded only with O(48f), Ti ion is thought to move away from the Gd vacancy in accordance with the outward relaxation of the O(48f) bonded with Ti ions.

This localized structural relaxation behavior around the Gd vacancy is regarded to be equivalent to imposing the local strain. The calculated O(48f) migration energies of each path near the Gd vacancy

| Migration specie | Relaxation distance (Å) |
|------------------|------------------------|
|                  | O(8b)      | O(48f)      | Gd          | Ti          |
| \( V_{\text{Gd}}^{-3} \) | -0.007     | +0.259      | -0.203      | +0.035      |
| \( V_{\text{Ti}}^{4-} \) | –          | +0.214      | -0.058      | -0.131      |
| \( V_{\text{O(48f)}^{2+}} \) | -0.045     | -0.178      | +0.274      | +0.272      |
| \( V_{\text{O(8b)}^{2+}} \) | –          | -0.212      | +0.070      | –           |
are summarized in parenthesis in Table III. It was found that the O(48f) migration energies increased by the Gd vacancy. In particular, the increase in the O(48f) migration energy along <110> was larger than that along <110> because of the different nature of the saddle point. The former migration requires O(48f) to pass between Gd and Ti ions. Owing to the presence of the local compressive strain for neighboring cations around the Gd vacancy, the distance between Ti and Gd vacancies was 3.648 Å at the saddle point, whose distance was 3.992 Å in the case of the isolated O(48f) migration. With regard to the O(48f) migration along <110>, the compressive strain was not as significant because O(48f) passes through a large Gd$_7$Ti$_3$ octahedron. For the triangle shaped configuration of Ti ions near the migrating O(48f) shown in Fig. 10 (b), the distance between Ti ions was no more than 0.1 Å compressed by the Gd vacancy. Thus, the increase in the migration energy was smaller for O(48f) along <110> than for that along <100>. These results suggest that cation cage size is also responsible for oxide-ion migration energy in pyrochlore.

The experimental activation energy of the ionic conduction in Gd$_2$Ti$_2$O$_7$ is reported to be 0.93 eV$^{45,47}$ and that from our experiment was 1.09 eV.$^{11}$ which values are larger than our calculated oxide-ion migration energies. Here, it can be considered that the experimentally measured activation energy$^{11,45,47}$ includes the effect of the Gd vacancy or other factors to induce the compressive strain.$^{39}$ Our previous experiment also showed that electrical conductivity decreased in air with increasing Gd deficiency and the apparent activation energy was increased to 1.17–2.44 eV depending on the Gd deficiency.$^{11}$ The present theoretical findings suggest that these decreases in electrical conductivity must have originated in the increase of O(48f) migration energy by the local compressive strain around Gd vacancies. Actually, the lattice constant of our experimental samples monotonically decreased with increasing Gd deficiency. It was shown that electrical conductivity in air reaches a minimum value at Gd composition, $x = 1.9$, then slightly increases as $x$ decreases in Gd$_x$Ti$_2$O$_{7−δ}$. As the Gd deficiency increases, the number of O(48f) vacancies should increase. Thus, it can be thought that the electrical conductivity of Gd$_x$Ti$_2$O$_{7−δ}$ was determined by the balance between the increase in the oxide-ion migration energy and the possible migration paths dependent on the Gd deficiency.

D. O(48f) migration in A$_2$B$_2$O$_7$ pyrochlore

1. O(48f) migration in Gd$_2$B$_2$O$_7$ pyrochlore

Finally, we will discuss the generalized rule of the O(48f) migration in A$_2$B$_2$O$_7$ pyrochlores by applying the present findings for Gd$_2$Ti$_2$O$_7$. As discussed in the preceding section, oxide-ion conduction in the actual pyrochlore system must be determined by various factors, including the strain due to the A-site deficiency, dopant substitution or structural disorder$^{50,51}$ and dominant vacancy formation in accordance with the chemical environment. To simplify the discussion, we will show the relationship between O(48f) migration energy and composition assuming the ideal pyrochlore structure for all A$_2$B$_2$O$_7$ composition. Different chemical compositions of course include the strain effect because combinations of A- and B-site elements systematically change the sizes of cation tetrahedrons, which must significantly affect the O(48f) migration energy. In particular, the migration path of O(48f)–8a is considered to be stabilized depending on the lattice constant or strain because the 8a site is enclosed in the B$_4$ cage. To confirm this idea, O(48f) migration energies in Gd$_2$Ti$_2$O$_7$, Gd$_2$Zr$_2$O$_7$, Gd$_2$Sn$_2$O$_7$ and Gd$_2$Hf$_2$O$_7$ were first investigated.

The obtained O(48f) migration energies of Gd$_2$Ti$_2$O$_7$, Gd$_2$Zr$_2$O$_7$, Gd$_2$Sn$_2$O$_7$ and Gd$_2$Hf$_2$O$_7$ are shown in Figs. 11. O(48f) migration energies along the <100> direction are plotted in Fig. 11 (a) as a function of the bond overlap population of B–O bonding. In accordance with the ionic radius of the B site element, the order of the calculated lattice constant was Gd$_2$Ti$_2$O$_7$ < Gd$_2$Hf$_2$O$_7$ ≲ Gd$_2$Sn$_2$O$_7$ < Gd$_2$Zr$_2$O$_7$. However, this order has no relation with the order of migration energies. In terms of the migration mechanism, O(48f) migration can be understood as the bending of the B–O bond. The migration energies of O(48f) along the <100> direction in Gd$_2$B$_2$O$_7$ (B=Ti, Zr, Sn, Hf) show clear dependence on the bond overlap population of the B–O bond. In addition, the ionic bonding strength of the B–O bond was also confirmed to follow the above relationship. Thus, the strength of the B–O bond is suggested to determine the O(48f) migration energy along the <001> direction.
On the other hand, O(48f) migration energies along the <110> direction of Gd₂Zr₂O₇, Gd₂Sn₂O₇ and Gd₂Hf₂O₇ showed negative values as shown in Fig. 11 (b). This result shows that the saddle point structures are more stable than the initial structures for Gd₂Zr₂O₇, Gd₂Sn₂O₇ and Gd₂Hf₂O₇. At the saddle point, migrating O(48f) was positioned near the 8a site, which corresponds to the V₈a–Oⁿ⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻¹⁻�

2. O(48f) migration in A₂Ti₂O₇ pyrochlore

Further, we investigated the O(48f) migration energy of A₂Ti₂O₇ compositions along with the same migration mechanism discussed above. Lanthanide elements from Ce to Er were selected as A-site cations. All f-electrons in lanthanide elements were assumed to be in the frozen core state and not to participate in the chemical bonding. Accordingly, spin polarization was not included because the magnetic moments of B-site cation and oxide-ion arise from the f-electrons of the A-site lanthanide elements. The resultant O(48f) migration energies of A₂Ti₂O₇ are plotted in Fig. 12 as a function of the ratio between the ionic radii of the B-site (=Ti ion) and the A-site cation (Ti/A). Linear interpolation can be valid because the migration energy of O(48f) in Gd₂Ti₂O₇ showed a linear dependence on the strain (lattice constant). As with the discussion of Figs. 11, O(48f) migration energies along the <110> direction for all compositions are almost constant and independent of Ti/A. In contrast, O(48f) migration energies along the <110> direction continuously decrease with increasing Ti/A from A = Ce to Gd and showing negative values from A = Tb to Er. Thus, the absolute values of these migration energies are plotted, which increase with increasing Ti/A from A = Tb to Er. Because O(48f) migration along the <110> direction crosses near the vacant 8a site, the negative value of the migration energy indicates that oxide-ion is more stable at the 8a site than at the 48f site. Therefore, the energy barrier of O(48f) migration along <110> corresponds to that of the O(8a) migration into V₈a along the <100> direction in the case of A = Tb to Er.
FIG. 12. O(48f) migration energies along the <100> and <110> directions in A₂Ti₂O₇ (A = Ce, Pr, Nd, Pm, Sm, Gd, Tb, Dy, Ho and Er) as a function of the ratio between the ionic radii of the A-site element and B-site element (B/A).

These results indicate that fluorite structure is energetically more stable than pyrochlore structure for A = Tb to Er of A₂Ti₂O₇. However, a complete pyrochlore–fluorite structural transition should not be possible because the available number of 8a sites is 1/6 of that of the 48f sites. As indicated in Fig. 11 (b), it can be considered that the size of the B₄ cage determines the stability of O(8a). On the other hand, lanthanide contraction surely decreased the lattice constant of pyrochlore, and the B₄ cage size also decreased. There seems to be a contradiction in the relationship between the decrease in B₄ cage size and the increase in the O(8a) stability. For the A₂Ti₂O₇ structure, a relatively small Ti₄ cage size is favorable for the stability of O(8a) because the Ti₄ cage size decreases with increasing ionic radius of the A-site cation while the stability of O(8a) decreases. At the saddle point of O(48f) migration along the <110> direction, the migrating oxide-ion draws close to Ti ion. It was found that the Ti–O bond length at the saddle point decreased with increasing ionic radius of the A-site cation and approached the initial Ti–O(48f) bond length of each compound. In particular, the coordination number of this migrating O(48f) was four at the saddle point structure of Ho₂Ti₂O₇ and Er₂Ti₂O₇ when the O(48f) migrates along <110>, which indicates that O(8a) is chemically stable in those compounds. However, this coordination number of migrating O(48f) was three in the other compounds, and the migrating O(48f) was located near the 8a site rather than within the Ti₄ cage. Thus, the stability of the O(8a) could be more appropriately determined by the balance between the Ti₄ cage size and Ti–O bond length (i.e., B/A). This is the reason why O(48f) migration energies are plotted as a function of Ti/A in Fig. 12. In short, we can propose that O(48f) migration along the <100> direction is governed by the strength of B–O bonding, whereas that along the <110> direction is determined by B/A in A₂B₂O₇ pyrochlore.

Here, we want to emphasis that Gd₂Ti₂O₇ must be the most favorable quasi-ternary pyrochlore compound for the ionic conduction. The present findings are quite consistent with the experimental investigation that Gd₂−ₓCaₓTi₂O₇ with x = 0.2 shows the highest oxide-ion conductivity within the pyrochlore compounds. Because the ionic radius of Ca is slightly larger than that of Gd, Ca substitution for Gd sites can introduce local expansion, which should lower the migration energy of O(48f). However, excessive expansion promotes the stability of the O(8a), which increases the migration energy of O(48f) by the other possible migration mechanism of O(8a)–V_O(48f). From these balances, it is thought that x = 0.2 is a suitable substitution content of Ca for Gd₂Ti₂O₇.

IV. SUMMARY AND CONCLUSIONS

In this study, we investigated the intrinsic defect formation and the O(48f) migration energy in Gd₂Ti₂O₇ from first-principles calculation and discussed the obtained results compared with our experiments. It was found that the vacancy formation energy of Gd is lower than that of Ti and is the dominant defect under the oxidation condition. In contrast, oxygen vacancy is dominant under the reduction condition. The oxygen vacancy formation energy was lower at the 48f site than at the 8b site because of the lower chemical binding strength. Moreover, the formation energy of the vacancy
complex showed that Gd vacancy is accompanied by oxygen vacancy at 48f. This indicates that A-site deficiency reduces the occupation of the 48f site, which is consistent with our experiment.

It was found that the Gd vacancy increases O(48f) migration energy because of the local compressive strain around the Gd vacancy, which inhibits O(48f) migration. This finding could well explain why our previous experiment showed a decrease in the electrical conductivity as increasingpressive strain around the Gd vacancy, which inhibits O(48f) migration. This finding could well deficiency reduces the occupation of the 48f site, which is consistent with our experiment.

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SUPPLEMENTARY MATERIAL

See supplementary material for the dynamical O(48f) migration behavior and strain dependent O(48f) migration energy in Gd$_2$Ti$_2$O$_7$.

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In accordance with the different nature of the saddle point of O(48f) along \(<100>\) and \(<110>\), migration energy of those paths are dependent on the strain. Migration energy of those paths decreased (increased) as tensile (compressive) strain, and changes were more significant for the path of O(48f) migration along \(<100>\). Calculated result of strain dependent migration energy is shown as Fig. S3 of supplementary material.