Analysis of atomic structure, magnetic ordering, and oxygen diffusion in oxygen deficient $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ perovskite: Toward rational catalysts design

Tadashi Ota^{1,*}, Musa Alaydrus¹, Hidetoshi Kizaki^{1,2,3} and Yoshitada Morikawa^{1,2,3,†}

¹Department of Precision Engineering, Graduate School of Engineering, Osaka University, 2-1, Yamadaoka, Suita, Osaka 565-0871, Japan

²Elements Strategy Initiative for Catalysis and Batteries (ESICB), Kyoto University, Goryo-Ohara, Nishikyo-ku, Kyoto 615-8245, Japan

³Research Center for Precision Engineering, Graduate School of Engineering, Osaka University, 2-1, Yamadaoka, Suita, Osaka 565-0871, Japan

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Mechanistic analysis of oxygen transfer in an atomic-scale structure is important for various applications, such as the three-way catalysts for treating NO_x in automotive exhaust and solid oxide fuel cell electrolyte materials. It has been shown that the $n = 2$ Ruddlesden-Popper phases $\text{Sr}_3\text{Fe}_2\text{O}_{7.0-\delta}$ have superior oxygen storage capacity compared to the conventional $\text{CeO}_2\text{-ZrO}_2$. Atomic structure, magnetic ordering, charged defects arising due to oxygen vacancies, and the effect of lattice parameters on the ionic transport in $\text{Sr}_3\text{Fe}_2\text{O}_{7.0-\delta}$ within the oxygen content of 5.75 to 7.0 were investigated by using DFT+ U calculations. In the case of $\text{Sr}_3\text{Fe}_2\text{O}_{6.0-7.0}$, the oxidation reaction energies were found to be almost independent of the initial oxygen content. We investigated the activation energies of oxygen diffusion by using the equilibrium and compressively strained lattice parameters for $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$. The activation energies were found to be nearly proportional to the volume of the unit cell; namely, as the volume of the unit cell increases, the activation energy decreases. It was found that in the oxygen diffusion process the activation energy increases as the bond length between iron and oxygen decreases and the bond length is minimum in the transition state, indicating that the iron-oxygen repulsive interaction is the origin of the activation energy. Moreover, in addition to the dominant migration pathway in $\text{Sr}_3\text{Fe}_2\text{O}_{6.0-7.0}$, a new migration pathway in $\text{Sr}_3\text{Fe}_2\text{O}_{5.75-6.0}$ was found.

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I. INTRODUCTION

Driven by growing global concern about climate change and emission of global warming gases, substantial efforts to develop new materials for building a sustainable future have been made [1]. Especially, since carbon dioxide (CO_2) and nitrogen oxides (NO_x) emissions have a large effect on the environment, stricter environmental regulations concerning decarbonization and NO_x emission are being imposed worldwide [2]. Enhancing the oxygen-diffusion properties and oxygen storage capacity in the perovskite and perovskite-like oxides has attracted much attention in regard to applications such as automotive three-way catalysis [3–10], cathodes and electrolytes of solid-oxide fuel cells (SOFCs) [11–21], and oxygen separation membranes [22–24]. To evaluate the performance of these applications, a variety of multiscale studies on topics ranging from atomic-scale oxygen transport processes in bulk as well as at surfaces and interfaces, to macroscale system reliability during operation have to

be performed. Quantum chemical calculations with density functional theory (DFT) help in understanding the essence of atomic-scale phenomena. Moreover, mechanistic analysis of oxygen migration and oxygen vacancy formation on the atomic scale can provide guidelines for designing highly active catalysts used in the above-mentioned applications.

Current state-of-the-art SOFCs typically operate at 700–850 °C and provide high power density and high-grade waste heat. However, long-term durability and low cost are still challenging issues facing more extensive utilization of SOFCs. Much attention has been directed toward developing low-temperature SOFCs operating at 400–650 °C, because they have improved durability and can reduce costs by using more economical materials. Even at the lowered operation temperatures, the high oxygen ionic diffusion property in SOFCs should be maintained to avoid the voltage drop and increase power generation efficiency. Thin yttria-stabilized zirconia (YSZ) is currently used for the electrolyte at an operation temperature $T > 700$ °C. To operate at temperatures below 700 °C, it is necessary to design new electrolyte materials with faster oxygen ionic conductivity and superior insulating property to replace YSZ [12].

The three-way catalysts used in automobile exhaust converters are used for converting the pollutant gases, such as NO_x , carbon monoxide (CO), and hydrocarbons (HCs), into environmentally less harmful emissions like nitrogen (N_2), CO_2 , and water (H_2O). Conventional three-way catalysts consist of an oxygen storage material such as solid $\text{CeO}_2\text{-ZrO}_2$,

*ota@cp.prec.eng.osaka-u.ac.jp

†morikawa@prec.eng.osaka-u.ac.jp

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the catalytically active noble metals like platinum (Pt), palladium (Pd), and rhodium (Rh), and a catalyst support such as Al_2O_3 . It should be noted here that the air-fuel ratio should be kept at the ideal stoichiometric air-fuel ratio. If the air-fuel ratio shifts from the ideal stoichiometric condition to a fuel-rich condition, purification rates for CO and hydrocarbons decrease, while under a fuel-lean condition, NO_x purification rate decreases. The actual air-fuel ratio in the exhaust gas always oscillates around the ideal air-fuel ratio and changes greatly depending on the driving mode such as startup. The oxygen storage material of solid $\text{CeO}_2\text{-ZrO}_2$ has a function of absorbing oxygen atoms under lean conditions and releasing oxygen atoms under fuel-rich conditions, in a manner that adjusts oxygen concentration according to the suitable catalytic-reaction conditions. As the environmental regulations become stricter, oxygen storage materials as alternatives to $\text{CeO}_2\text{-ZrO}_2$ have been extensively researched. In particular, perovskite oxides and perovskite-derived oxides have been reported to have the high performance as the oxygen storage materials.

Recently, it was experimentally revealed that $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ with a layered Ruddlesden-Popper oxide has higher oxygen storage and release abilities than the conventional automotive catalysts $\text{CeO}_2\text{-ZrO}_2$ and shows structural durability under severe reduction conditions [5–7]. In our previous study, we used DFT to investigate oxygen-ionic-transport properties, vacancy configurations, and electronic structures of $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ with oxygen content from 6.0 to 7.0 [25]. The results of the investigation revealed that the activation energy of oxygen diffusion in $\text{Sr}_3\text{Fe}_2\text{O}_6$ is 1.35 eV, which represents a higher migration barrier than that of $\text{Sr}_3\text{Fe}_2\text{O}_{6.25-6.75}$ by more than 0.26 eV. We also revealed that the addition of an O3 atom between the bilayers of FeO_6 octahedra gives rise to the Jahn-Teller distortion, which reduces the activation energy of oxygen ionic diffusion in $\text{Sr}_3\text{Fe}_2\text{O}_{6.25-6.75}$ compared to that in $\text{Sr}_3\text{Fe}_2\text{O}_{6.0}$. Other experimental studies have recently shown that the oxygen nonstoichiometric range is found to be extended when the oxygen content is from 5.80 to 6.71 by the partial substitution of iron by nickel in $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$, while the oxygen storage and release in $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ without substitution occurs when the oxygen content is from 5.98 to 6.73 [8,9]. Another experimental study reported the synthesis of $\text{Sr}_3\text{Fe}_2\text{O}_5$ with a spin ladder system by the reaction of $\text{Sr}_3\text{Fe}_2\text{O}_7$ with calcium hydride CaH_2 [26]. The results of that experiment show the feasibility of oxygen reduction below the oxygen content of 6.0. The electronic structure of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ significantly differs from that of $\text{Sr}_3\text{Fe}_2\text{O}_{6.0}$ due to the formation of vacancies at the equatorial O1 sites of FeO_6 octahedron. Furthermore, in previous studies on this material, the effect of unit-cell lattice parameters was not investigated, although it was pointed out that both compressive and tensile strain affect the properties of oxygen migration in other perovskite oxides [27,28]. In this study, we used DFT+ U calculations to investigate the atomic structure, the magnetic ordering, the charged defects arising due to oxygen vacancies, and the effect of lattice parameters on the ionic transport in the case of oxygen content from 5.75 to 7.0.

II. METHOD

All the calculations were performed based on spin-polarized DFT+ U theory using the STATE (Simulation

Tool for Atom TEchnology) program package with ultra-soft pseudopotentials. The STATE program package has been successfully used for both bulk and surface structures with metal or semiconductor properties [29,30]. Electronic structures were calculated by using DFT+ U under a generalized gradient approximation (GGA) method with the Perdew-Burke-Ernzerhof (PBE) exchange correlation [31–36]. The on-site Coulomb U and exchange J parameters for localized Fe 3d electronic states were chosen as $U = 5$ eV and $J = 1$ eV. Energy cutoffs for the wave functions and augmentation charge were 25 and 225 Ry, respectively. The effects of expanded energy cutoff and augmentation charge on lattice relaxation in $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$ were also investigated. The expanded cutoff and augmentation charge, which were increased to 36 and 400 Ry, respectively, result in the small difference between lattice parameters of 0.2% and 0.4% for the a and c axes, respectively. A $\sqrt{2} \times \sqrt{2} \times 1$ supercell was used to investigate the stable spin configurations and the ground-state structures. In the calculations of the formation energies of charged defects arising due to oxygen vacancies, a $2 \times 2 \times 1$ supercell was used to obtain a greater distance between charged oxygen vacancies and check the unit-cell dependence. To calculate a $\sqrt{2} \times \sqrt{2} \times 1$ supercell, the Brillouin zone was sampled with $8 \times 8 \times 2$ Monkhorst-Pack grids [37]. The atomic structure of $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ has the basis of the $n = 2$ Ruddlesden-Popper $A_{n+1}B_nC_{n+1}$ phase. The space group is tetragonal $I4/mmm$ (No. 139).

In this study, the generalized direct inversion in the iterative subspace (GDIIS) scheme was used for all atomic relaxations, and the lattice unit-cell parameters, namely, a and c , were also optimized. The lattice parameters were calculated by fitting the a and c axes at nine points (3×3) with a quadratic function, instead of calculating the Pulay stress analytically. It was assumed that the structure maintains a tetragonal symmetry during the atomic and lattice relaxations. The calculated atomic structures and lattice parameters are shown in Fig. 1 and Fig. 3, respectively. In terms of the magnetic configurations, the antiferromagnetic ordering with G type (G-AFM), which has the antiferromagnetic iron spins for both intra- and interlayers, has been experimentally and theoretically identified as the ground state for $\text{Sr}_3\text{Fe}_2\text{O}_{6.0}$ [25,38]. As shown in Fig. 2, to investigate the spin configuration in $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ in the case of the assumption of collinear magnetic configurations, G-AFM, the antiferromagnetic orderings with C-type (C-AFM), A-type (A-AFM), and ferromagnetic (FM) ordering were calculated. The assumption concerning A-AFM ordering is explained as follows. The crystal structure of $\text{Sr}_3\text{Fe}_2\text{O}_{7.0-\delta}$ is a Ruddlesden-Popper structure containing a bilayer composed of a $\text{SrFeO}_{3.0-\delta}$ perovskite layer separated by a SrO rocksalt layer. The perovskite layer, with a tetrahedron FeO_5 structure, in which all O3 sites are empty and all O1 sites are occupied by oxygen, has been found to be G-AFM ordering in $\text{Sr}_3\text{Fe}_2\text{O}_{6.0}$ [25,38]. In the case of $\text{Sr}_3\text{Fe}_2\text{O}_{6.25-7.0}$, when the O3 sites of the perovskite layer are partially occupied, the in-plane spin configuration of the iron atoms becomes FM ordering. As the occupancy of the O3 sites increases, the out-of-plane spin configuration of the iron atoms between the O3 sites also becomes FM ordering [25]. Spin interaction between the perovskite layers through the SrO rocksalt layer was found to be weak. A perovskite

FIG. 1. Atomic configurations of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$, $\text{Sr}_3\text{Fe}_2\text{O}_{6.0}$, and $\text{Sr}_3\text{Fe}_2\text{O}_{7.0}$ with $n = 2$ Ruddlesden-Popper. Strontium, iron, and oxygen atoms are shown as green, yellow, and red spheres, respectively. $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ (X) has vacancies at one O1 and all O3 sites in a $\sqrt{2} \times \sqrt{2} \times 1$ supercell. $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ (Y) has vacancies at one O2 and all O3 sites. $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ (Z) has vacancies at two O1 sites, and one O3 site is occupied by an oxygen atom. As for $\text{Sr}_3\text{Fe}_2\text{O}_{6.0}$, all O3 sites are unoccupied, while as for $\text{Sr}_3\text{Fe}_2\text{O}_{7.0}$, those sites are fully occupied.

layer with all O3 sites empty and all O1 sites occupied keeps G-AFM ordering even if adjacent perovskite layer is A-AFM ordering with partially occupied O3 sites. Hereafter, it is therefore assumed that the layer with FeO_5 structure, where all the O3 sites are empty and all the O1 sites are completely occupied maintains the G-AFM ordering even in the A-AFM spin configuration, as shown in Fig. 2.

The Gibbs free energy of formation ΔG_{form} can be expanded as

$$\Delta G_{\text{form}} = \Delta E_{\text{form}} - T \Delta S_{\text{form}} + P \Delta V_{\text{form}}, \quad (1)$$

where ΔE_{form} is change of total energy due to introduction of an oxygen vacancy [see Eq. (2)], ΔS_{form} is formation entropy which is primarily contributed by a vibration effect, and ΔV_{form} is volume change when an oxygen vacancy is introduced. Oxidation reaction energy ΔE_{form} based on a per- O_2 -molecule basis was calculated as previously reported

FIG. 2. Relative total energies of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ (X), (Y), and (Z) with different magnetic configurations are shown in the upper panel. Total energy of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ (X) with G-AFM ordering is set to zero. G-AFM, C-AFM, A-AFM, and FM magnetic configurations of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ (X), (Y), and (Z) are shown in the lower panel.

[15,39] as

$$\Delta E_{\text{form}} = \frac{E(\text{MO}_{x+0.25}) - E(\text{MO}_x) - \frac{0.25}{2} \mu(\text{O}_2)}{\frac{0.25}{2}}, \quad (2)$$

where MO_x is $\text{Sr}_3\text{Fe}_2\text{O}_x$, where x is between 5.75 and 7.0. Since the supercell used in our calculations has four formula units, $\text{O}_{0.25}$ is equivalent to one oxygen atom per supercell. It was previously found that calculation of the oxygen molecule includes the overbinding error in the DFT with GGA calculation [15,39]. In this study, the calculated oxidation reaction energy was downshifted by the correction $\Delta h_{\text{O}_2}^0 = 1.36 \text{ eV}/\text{O}_2$ in order to fit to the experimental chemical potential [39]. As for the formation entropy ΔS_{form} , we approximated the Gibbs energy by the corresponding ground-state energies at 0 K. We do not consider the phonon contribution to Gibbs free energy, which we expect to be the same order as $\sim 0.1 \text{ eV}$ in the case of BaZrO_3 [40]. However, we considered the effect of entropy due to variations of oxygen vacancy configurations on the oxidation reaction energy of $\text{Sr}_3\text{Fe}_2\text{O}_{6.0-7.0}$. In terms of volume change ΔV_{form} , according to the calculated volumes listed in Table I, the change of volume caused by the release of oxygen atoms is very small, namely, $0.1-2.8 (\text{\AA}^3)$, at oxygen content from 5.75

TABLE I. Properties of $\text{Sr}_3\text{Fe}_2\text{O}_{7.0-\delta}$ ($5.75 \leq 7.0 - \delta \leq 7.0$) in ground state compared with experimental results. Supercell volumes, bond lengths around iron atoms, angles of Fe-O-Fe atoms in the planar and perpendicular directions, and energy gaps are shown. Calculated bond lengths and angles represent the local properties, namely, the local positions where oxygen atoms are extracted or added at O1 and O3 sites. Experimental values refer to the following references: (a) Ref. [47], (b) Ref. [8], (c) Ref. [48], (d) Ref. [6], (e) Ref. [50], and (f) Ref. [38]. Experimental magnetic orderings are from Ref. [38].

Property	7.0 - δ										
	5.75	6.0		6.25		6.50		6.75		7.0	
	Calc.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.
V_{cell} ($\text{\AA}^3$)	318.49	315.94	303.41 ^a 303.90 ^b	316.09	(303.07) ^a (316.75) ^c	316.49	(302.58) ^a	313.69	301.68 ^a 301.20 ^d	311.77	299.15 ^a
$d(\text{Fe-O1})$ ($\text{\AA}$)	2.02($\times 2$) 1.95($\times 1$)	2.01($\times 4$)	1.98 ^a	2.06($\times 4$)	1.98 ^c	2.06($\times 4$)	(1.94) ^a	2.04($\times 4$)	1.94 ^a	1.96($\times 4$)	1.93 ^a
$d(\text{Fe-O2})$ ($\text{\AA}$)	1.99	1.91	1.89 ^a	1.97	1.96 ^c	1.97	(1.93) ^a	1.94	1.93 ^a	1.97	1.94 ^a
$d(\text{Fe-O3})$ ($\text{\AA}$)				1.93	2.07 ^c	1.93	(2.00) ^a	1.94	1.98 ^a	1.99	1.96 ^a
$d(\text{Fe-Fe})_{\text{xy}}$ ($\text{\AA}$)	3.97	3.95		3.95		3.95		3.93		3.91	
$d(\text{Fe-Fe})_z$ ($\text{\AA}$)	4.31	4.19		3.86		3.86		3.88		3.98	
				4.32		4.30		4.32			
$\alpha(\text{Fe-O1-Fe})$ (deg)	160($\times 2$) 126($\times 1$)	157($\times 2$) 158($\times 2$)		166($\times 2$) 167($\times 2$)		168($\times 4$)		167($\times 4$)		178($\times 4$)	
$\alpha(\text{Fe-O3-Fe})$ (deg)				179		179		180		180	
Magnetic ordering	AFM	AFM	AFM	AFM	AFM	AFM	AFM	FM	AFM	FM	helical
Magnetic ordering _⊥	AFM	AFM	AFM	FM	FM	FM	FM	FM	FM	FM	helical
E_{gap} (eV)	0.99	2.13	2.3 ^e	0.52	insulator	0.64	insulator	0	insulator ^f	0	insulator ^f

to 7.0. Since pressure is assumed to be 1 atm, the $P\Delta V_{\text{form}}$ term in Eq. (1) is also a very small value and assumed to be negligible. To compare the calculated oxidation reaction energy with the experimentally measured value, the chemical potential of an oxygen molecule, which is fixed by the condition of thermodynamic stability in the surrounding gas phase, was estimated. The dependence of temperature and pressure on chemical potential is described as

$$\mu_{\text{O}_2}(T, p_{\text{O}_2}) = \tilde{\mu}_{\text{O}_2}(T, p^0) + k_{\text{B}}T \ln \left(\frac{p_{\text{O}_2}}{p^0} \right), \quad (3)$$

where $\tilde{\mu}_{\text{O}_2}(T, p^0)$ is based on the experimental values taken from a thermodynamic table at $p^0 = 1$ atm [41,42].

Formation energy E_f^Q of an oxygen defect in charge state Q ($Q = 0, \pm 1, \pm 2$) is defined as [43–45]

$$E_f^Q = (E_D^Q - E_X^0) + Q(\varepsilon_F + \varepsilon_v) - \sum_s (n_s^D - n_s^X) \mu_s, \quad (4)$$

where E_D^Q is the calculated total energy containing the defect D . E_X^0 is the corresponding total energy for a perfect crystal using the equivalent supercell. ε_F is measured from the valence-band top ε_v , whereas ε_v is relative to the vacuum. μ_s is the corresponding chemical potential of the atomic species s . n_s^D and n_s^X are the number of atoms with and without a defect in the supercell.

Relative formation energy between different charge states is defined as

$$E_f^{\pm 1} - E_f^0 = (E_D^{\pm 1} - E_D^0) \pm (\varepsilon_F + \varepsilon_v). \quad (5)$$

The defects are restricted to a single oxygen vacancy so that μ_{O} is not required to obtain relative formation energies of the defect. Here, it is assumed that minus ε_v is the first ionization

energy of a semiconductor and is expressed as

$$\varepsilon_v = E_{\text{crys}}^0 - E_{\text{crys}}^{+1}. \quad (6)$$

E_{crys}^0 is the total energy of the perfect crystal and E_{crys}^{+1} is the highest occupied state being empty. Equation (6) is evaluated by the supercell model as

$$E_{\text{crys}}^0 - E_{\text{crys}}^{+1} = E_X^0 - E_X^{+1}. \quad (7)$$

Relative formation energy between positive and neutral charge states is given as

$$E_f^{+1} - E_f^0 = (E_D^{+1} - E_X^{+1}) - (E_D^0 - E_X^0) + \varepsilon_F. \quad (8)$$

Hereafter, Eq. (8) along with Eq. (4) is used to evaluate the relative formation energy of charged defects. As for the figures in this paper, we used Visualization for Electronic and Structural Analysis (VESTA) software [46].

III. RESULTS AND DISCUSSION

A. Crystal structures and magnetic properties of $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$

As many experimental studies have previously reported [5,6,47,48], the crystal structures of $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ are modeled by using the tetragonal symmetry $I4/mmm$ space group. It was reported that $\text{Sr}_3(\text{Fe}, M)_2\text{O}_{7.0-\delta}$ with Fe substitution by other transition metals of M ($M = \text{Ni}, \text{Co}, \text{and Mn}$) has tetragonal symmetry in the oxygen content of 5.75–6.0 as well as 6.0–6.7 [8,49]. Therefore, in this study, it is assumed that the layered perovskite structures with the tetragonal symmetry are maintained at the oxygen contents of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75-7.0}$. The structure of $n = 2$ Ruddlesden-Popper phase $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ has three crystallographically inequivalent sites as the positions of oxygen atoms and oxygen vacancies, as shown in Fig. 1. In this structure, O1 sites are located at the equatorial positions

FIG. 3. Calculated and experimental lattice parameters in $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ are represented by blue solid and black dashed lines, respectively. Experimental values are taken from Ref. [47]. Experimental values for $\text{Sr}_3\text{Fe}_2\text{O}_{6.25}$ and $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$ are linearly interpolated using the values from Ref. [47].

of FeO_6 octahedra. O2 sites are located at the apical site in the rocksalt layer. O3 sites are represented at the apical positions between bilayers of FeO_6 octahedra. Three structures of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ (X)–(Z) in the upper panel of Fig. 1 are considered as the atomic configurations in $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$, because they are important in regard to the oxygen ionic transport in $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$, as discussed in the last subsection. The structure of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ (X) has vacancies at the equatorial O1 sites of FeO_6 octahedra, as well as the apical O3 sites between bilayers of FeO_6 octahedra. The structure of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ (Y) has vacancies at the apical O2 sites in the rock-salt layer, as well as the apical O3 sites, considering the structure after the oxygen ionic diffusion from O2 sites to O1 sites. The structure of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ (Z) has vacancies at the equatorial O1 sites and partial occupation at the apical O3 sites between bilayers of the FeO_6 octahedra after migration of oxygen atoms from O1 sites to O3 sites. In previous research, the oxygen occupancy at the O1, O2, and O3 sites and stable magnetic configurations in $\text{Sr}_3\text{Fe}_2\text{O}_{6.0-7.0}$ were investigated by DFT+ U and experiments [6,25]. In the case of $\text{Sr}_3\text{Fe}_2\text{O}_7$, the O1, O2, and O3 sites are fully occupied as shown in the lower right panel of Fig. 1. When $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ is reduced at the oxygen content of 6.0–7.0, the O3 oxygen atoms between FeO_6 layers are extracted. In the case of $\text{Sr}_3\text{Fe}_2\text{O}_6$, the O3 site is completely vacant, and the O1 and O2 sites are fully occupied. The stable magnetic configuration of $\text{Sr}_3\text{Fe}_2\text{O}_6$ is G-AFM ordering, and that of $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ is likely to be A-AFM or FM orderings according to collinear calculation as the oxygen content increases from 6.0 to 7.0 [25]. To identify the preferred occupation site of oxygen atoms and the magnetic configuration in $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$, the relative total energies of the three $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ structures with different magnetic configurations were calculated as shown in the upper panel of Fig. 2. Here, as for the magnetic configurations of

$\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$, G-AFM, C-AFM, A-AFM, and FM spin configurations are considered for $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ as shown in the lower panel of Fig. 2. The calculated relative total energies reveal that $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ (X) with vacancies at O1 and O3 sites is more stable than $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ (Y) and $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ (Z) by 0.61 and 0.79 eV, respectively. As for the magnetic ordering, the G-AFM configuration was found to be the most stable among the considered magnetic orderings for $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ (X)–(Z), and C-AFM was found to be the next most stable. The present study indicates that when the oxygen reduction of $\text{Sr}_3\text{Fe}_2\text{O}_6$ to $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ occurs, oxygen atoms at O1 sites are extracted from $\text{Sr}_3\text{Fe}_2\text{O}_6$ and the magnetic configurations are likely to be the antiferromagnetic ordering in the FeO_2 layers of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75-6.0}$.

Lattice parameters a and c and the properties of the atomic and electronic structures of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75-7.0}$ were calculated and compared with the experimental values as shown in Fig. 3 and Table I, respectively. The trends of calculated lattice parameters are consistent with those of experimental measurements. The calculated lattice parameters of a and c are larger than the experimental values by +1.4%–1.8% and +1.0%–1.1%, respectively. Lattice parameter c decreases as the oxygen content increases from 5.75 to 6.0. When the oxygen content increases from 5.75 to 6.0, the bond length of $d(\text{Fe-Fe})_z$ decreases by 0.12 Å (4.31 Å $\rightarrow$ 4.19 Å), which largely contributes to the decrease of 0.16 Å (20.382 Å $\rightarrow$ 20.222 Å) in the lattice parameter c . Both lattice parameter c and bond length of $d(\text{Fe-Fe})_z$ increase as oxygen content increases from 6.0 to 7.0. The increase of lattice parameter c is related to the fact that the oxygen atoms are added at the apical O3 site between the bilayer of the FeO_6 octahedron when the oxygen content increases from 6.0 to 7.0.

Lattice parameter a decreases as the oxygen content increases from 5.75 to 7.0. The trend in the lattice parameter

FIG. 4. Oxidation reaction energies and energy differences for the oxygen contents in $\text{Sr}_3\text{Fe}_2\text{O}_{5.75-7.0}$. Solid bars represent the calculation results obtained by using optimized lattice parameters as shown in Fig. 3, while dashed lines represent results obtained with fixed lattice parameters based on Ref. [25]. Oxidation reaction energy ΔG is calculated by using Eq. (1). Dependence of $\mu_{\text{O}_2}(T, p_{\text{O}_2})$ is shown as a pressure scale at $T = 600, 900$, and 1000 K based on Eq. (3). Total and partial densities of states in $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ and $\text{Sr}_3\text{Fe}_2\text{O}_{6.00}$ are given in the right panel. t_2 and e states of iron atoms are represented by red and black lines, respectively.

a corresponds with that of bond length of $d(\text{Fe-O1})$ in $\text{Sr}_3\text{Fe}_2\text{O}_{5.75-7.0}$. Bond length of $d(\text{Fe-O1})$ in $\text{Sr}_3\text{Fe}_2\text{O}_{6.0}$ is $2.01 \text{ \AA}$, while that in $\text{Sr}_3\text{Fe}_2\text{O}_{7.0}$ is $1.96 \text{ \AA}$, which is shorter by $0.05 \text{ \AA}$ (2.6%), as shown in Table I. When the oxidation reaction from $\text{Sr}_3\text{Fe}_2\text{O}_{6.0}$ to $\text{Sr}_3\text{Fe}_2\text{O}_{7.0}$ occurs, the valence number of the iron atom is changed from Fe^{3+} to Fe^{4+} . Based on the experimental results, the ionic radius of the iron atom with high spin state is $0.785 \text{ \AA}$ for Fe^{3+} , while it is $0.725 \text{ \AA}$ for Fe^{4+} [51]. Ionic radius of Fe^{3+} is larger than that of Fe^{4+} by $0.06 \text{ \AA}$ (8.2%). The difference in the ionic radii of Fe^{3+} and Fe^{4+} is consistent with the difference in bond lengths of $d(\text{Fe-O1})$ of $\text{Sr}_3\text{Fe}_2\text{O}_{6.0}$ and $\text{Sr}_3\text{Fe}_2\text{O}_{7.0}$. Therefore, the change in the oxidation state of iron atoms is likely to contribute to the decrease in the lattice parameter a in $\text{Sr}_3\text{Fe}_2\text{O}_{5.75-7.0}$.

The calculated energy gap of $\text{Sr}_3\text{Fe}_2\text{O}_{6.0}$ also agrees well with the experimentally measured value. Moreover, the calculated results of atomic and electronic structures agree with experimental results for $\text{Sr}_3\text{Fe}_2\text{O}_{6.0-6.75}$. The electronic structure of $\text{Sr}_3\text{Fe}_2\text{O}_{6.75-7.0}$ was shown to be a small-gap insulator by the experimental measurements; on the contrary, the calculations predicted it to be metallic and could not reproduce the experimental results for $\text{Sr}_3\text{Fe}_2\text{O}_{6.75-7.0}$ according to collinear magnetic calculations as discussed previously [25].

1. Reduction and oxidation reaction in $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$

To clarify the oxygen storage capacity, the oxidation reaction energies of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75-7.0}$ were calculated as shown by the solid bar in Fig. 4. If oxidation reaction energy is more negative, oxidation is the preferred reaction; in other words,

the reduction reaction is more difficult. Oxidation reaction energies ΔG were calculated by using Eq. (1) and the total energies of structures with relaxed lattice parameters and stable magnetic configurations. In the case of $\text{Sr}_3\text{Fe}_2\text{O}_{6.0-7.0}$, the oxidation reaction energies are almost independent of the oxygen content, as shown in gaps₁₋₃ of Fig. 4. A topotactic phase transformation in $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ is observed at the oxygen content of $6.0-6.7$ in the experiment; namely, $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ can be easily reduced or oxidized to change the oxygen content between $6.0-6.7$, indicating that the oxidation reaction energy is nearly constant in this oxygen content region, and that finding agrees with the calculation results.

In our previous study, the lattice parameters of $\text{Sr}_3\text{Fe}_2\text{O}_{6.0-6.75}$ and $\text{Sr}_3\text{Fe}_2\text{O}_{7.0}$ were determined from the experimental values of $\text{Sr}_3\text{Fe}_2\text{O}_{6.0}$ and $\text{Sr}_3\text{Fe}_2\text{O}_{7.0}$, respectively. Namely, the lattice parameters used in our previous study are given as follows: a and c values for $\text{Sr}_3\text{Fe}_2\text{O}_{6.0-6.75}$ were fixed to be $3.89 \text{ \AA}$ and $20.04 \text{ \AA}$, respectively. As for $\text{Sr}_3\text{Fe}_2\text{O}_{7.0}$, a and c values were fixed to $3.85 \text{ \AA}$ and $20.15 \text{ \AA}$, respectively [25,47,52]. Oxidation reaction energies calculated by using these experimental lattice parameters are shown by dashed lines in Fig. 4. The oxidation reaction energy obtained with experimental lattice parameters for oxygen content between $6.75-7.0$ is about -2.00 eV , while that for oxygen content between $6.5-6.75$ is reduced to -2.55 eV , and that for the oxygen content between $6.25-6.5$ first increased to -2.31 eV and then slightly increased to -2.23 eV , indicating that the reduction of $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ becomes somewhat difficult at oxygen content between $6.5-6.75$. The relaxation of lattice parameters

reduces the differences in oxidation reaction energies to below 0.1 eV and changes energy gap₃ in oxidation reaction energies of $\text{Sr}_3\text{Fe}_2\text{O}_{6.5-7.0}$ by 0.54 eV (0.56 eV $\rightarrow$ 0.02 eV) at most, as shown in Fig. 4, indicating the importance of the relaxation of the lattice unit-cell parameters in regard to oxidation reaction energies.

Oxidation reaction energy of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75-6.0}$ is found to be lowered significantly to -9.5 eV, namely, much more negative than that of $\text{Sr}_3\text{Fe}_2\text{O}_{6.0-7.0}$, as shown in Fig. 4. This result shows that $\text{Sr}_3\text{Fe}_2\text{O}_6$ has a large energy barrier to be reduced to $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$. Total and partial density of states of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ and $\text{Sr}_3\text{Fe}_2\text{O}_6$ are shown in the right panel of Fig. 4. t_2 and e states of iron atoms are represented by red and black lines, respectively. Partial density of states of iron atoms in $\text{Sr}_3\text{Fe}_2\text{O}_6$ has large filling of the majority spin and shows the high-spin electronic $\text{Fe}^{3+}(d^5)$ configuration. The d orbitals split into t_2 and e states in an octahedral field. Due to the reduction of symmetry related with the vacancy at O3 site, the $d_{3z^2-r^2}$ state is downshifted, and the $d_{x^2-y^2}$ state is the highest near the Fermi level. In the case of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$, when an oxygen atom is extracted from the O1 site in the y direction, as shown in the lower right panel of Fig. 4, the oxidation state of iron is $\text{Fe}^{2+}(d^{5+\delta})$. As for the majority spin, the electronic structure is basically the same as that in $\text{Sr}_3\text{Fe}_2\text{O}_{6.0}$; namely, all d up-spin states are occupied. On the contrary, as for the minority spin, because of the lowering of the symmetry due to the formation of oxygen vacancies at the O1 site, the d_{yz} and $d_{x^2-y^2}$ states are hybridized and shifted down below the Fermi level. Lee *et al.* have theoretically reported that the oxygen vacancy formation energy for the $\text{LaFeO}_3(\text{Fe}^{3+})$ bulk system is 4.5 eV (normalized as per O atom), which is consistent with our estimated reaction energies of -9.5 eV for the O_2 molecule in $\text{Sr}_3\text{Fe}_2\text{O}_{5.75-6.0}$ [15]. The significantly more negative reaction energies of oxidation of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ oxidation to $\text{Sr}_3\text{Fe}_2\text{O}_{6.0}$ is related to increasing oxygen vacancy formation energy when going from Fe^{3+} is reduced to Fe^{2+} in bulk oxides.

2. Relative formation energy of charged defect

Relative formation energy of an oxygen defect between positively charged ($q = +1$) and neutral states as a function of Fermi level in the energy gap is shown in Fig. 5(a). Relative formation energy of an oxygen defect was calculated for $\text{Sr}_3\text{Fe}_2\text{O}_{5.75-6.0}$. The calculation result shows that positively charged state becomes stable at the position of ϵ_F from 0 to 1.12 eV above the valence band top ϵ_v . The neutral state is found to be the most stable in the range of ϵ_F over 1.12 eV. Iron atoms at Fe1 and Fe3 sites adjacent to vacancies and the oxygen atoms around the iron atoms are illustrated in Fig. 5(b). The total and partial density of states in $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ with neutral and charged defects in $q = +1$ state are shown in Figs. 5(c) and 5(d), respectively. The t_2 and e states of iron atoms are represented by red and black lines, respectively. In the case of neutral state, the d orbitals in the majority spin are fully occupied, while one hybridized state between the $d_{x^2-y^2}$ and d_{yz} states is occupied in the minority spin. Therefore, the iron atoms of both Fe1 and Fe3 sites near the oxygen vacancies are Fe^{2+} . In the case of charged defects in $q = +1$ state, the hybridized state in the minority spin of

the Fe3 atom is extracted above the Fermi level, while the d orbitals in the majority spin remains to be fully occupied. On the contrary, the electronic structure of the Fe1 atom is almost unchanged from that in the neutral state; namely, the d orbitals are fully occupied in the majority spin and the hybridized state is occupied in the minority spin. The oxidation state of iron at the Fe3 site is Fe^{3+} , while that at the Fe1 site remains Fe^{2+} as well as the case of $q = 0$. Therefore, the electronic structure of iron atoms becomes asymmetrical around the oxygen vacancies. Although we examined the oxygen defect with doubly positively charged state, the calculation was difficult to converge. We expect the doubly charged state to be more unstable than the singly charged defect in $\text{Sr}_3\text{Fe}_2\text{O}_{5.75-6.0}$. Although the previous study of charged defects in BaZrO_3 showed that an oxygen defect in the doubly positively charged state becomes stable, $\text{Sr}_3\text{Fe}_2\text{O}_{5.75-6.0}$ is found to have singly positively charged defect [40].

B. Oxygen ionic transport in $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$

Activation energies of oxygen migration with different lattice parameters and the partial density of states for the initial states, the final states, and the transition states in the case of $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$ and $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ were investigated, as shown in Fig. 6 and Fig. 8. Activation energies were calculated by the climbing-image nudged-elastic-band (CI-NEB) method. Here, the two migration paths of $\text{O1} \rightarrow \text{O3}$ and $\text{O2} \rightarrow \text{O1}$ paths, which are the most plausible and the second most plausible migration paths in $\text{Sr}_3\text{Fe}_2\text{O}_{7.0-\delta}$ according to our previous research, are considered [25]. The obtained activation energies and the electronic structures are analyzed in more detail in the following subsections.

I. $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$

As for the oxygen migration in $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$, the calculated activation energies are 0.92 eV and 0.91 eV for the $\text{O1} \rightarrow \text{O3}$ and $\text{O2} \rightarrow \text{O1}$ paths, respectively. These values are smaller than those in our previously calculated values [25]. Activation energies obtained by using relaxed and compressive-strained lattice parameters as well as the lattice parameters with either the a axis or c axis compressed are shown in the lower left of Fig. 6. The movement of ions during oxygen diffusion and the bond length of iron and oxygen ions in the transition state are also shown in the upper right and lower right of Fig. 6, respectively. The migration barrier of the $\text{O1} \rightarrow \text{O3}$ and $\text{O2} \rightarrow \text{O1}$ paths is decreased by the effect of lattice relaxation by 0.17 eV ($1.09 \rightarrow 0.92$) and 0.19 eV ($1.10 \rightarrow 0.91$), respectively [25]. This result also indicates the importance of the relaxation of the lattice parameters. According to a previous theoretical research, the effect of the lattice parameters on the activation energies is 0.16 to 0.27 eV in the case of Sm-doped ceria for 4% change on the lattice parameters [28], while the change in lattice parameters of 1.3%–1.5% influences the activation energy of $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ by 0.17–0.19 eV. When the oxygen atom diffuses along the $\text{O1} \rightarrow \text{O3}$ and $\text{O2} \rightarrow \text{O1}$ paths, the oxygen and strontium ions overlap, affecting the atomic configuration of strontium and iron ions around the migrating oxygen ions. As the oxygen ion approaches the strontium ion, the strontium ion moves away from the oxygen ion. The bond length of iron and oxygen ions is shortened during the

FIG. 5. (a) Relative formation energy of an oxygen defect depending on Fermi energy for an oxygen point defect in $\text{Sr}_3\text{Fe}_2\text{O}_{5.75-6.0}$. Charged ($q = +1$) and neutral defects are shown. (b) Structure of vacancy positions in $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ with a $2 \times 2 \times 1$ supercell. Fe1 and Fe3 are the sites adjacent to vacancies. (c) Total and partial densities of states in $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ with neutral and charged defects in $q = +1$ state. Partial densities of states are shown for Fe1 and Fe3 adjacent to vacancies and the oxygen atoms around the iron atoms. t_2 and e states of iron atoms are represented by red and black lines, respectively.

diffusion process. Compared to the compressed lattice parameters, the relaxed lattice parameters facilitate the movement of strontium and iron ions and contribute to the reduction of the activation energy. It was confirmed that the bond length of iron and oxygen ions is minimized at the corresponding transition state, as shown in the lower right of Fig. 6. In the case of relaxed lattice parameters, the optimized bond length of iron and oxygen ions causes the lower activation energies in the oxygen migration. The influence of oxygen migration on the atomic configurations and the analysis of the interatomic distances of strontium, oxygen, and iron ions are discussed in the Supplemental Material [53] (see Figs. S1

and S2). The relationship between the volume of a supercell and the activation energy for the $\text{O1} \rightarrow \text{O3}$ and $\text{O2} \rightarrow \text{O1}$ paths in $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$ is shown in Fig. 7. We confirmed that the volume and the activation energy have a linear relationship. As the volume of the supercell increases, the activation energy decreases for both oxygen migration paths.

In terms of the electronic structures of $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$, the electronic structures of the $\text{O1} \rightarrow \text{O3}$ path have energy gaps during the oxygen migration, while those of $\text{O2} \rightarrow \text{O1}$ become metallic in the transition state, as shown in Fig. 8. In the electronic structure of iron (see the Fe2 site in the upper panel of Fig. 8) at the initial state, the $d_{x^2-y^2}$ state is

FIG. 6. Activation energies of $\text{O1} \rightarrow \text{O3}$ and $\text{O2} \rightarrow \text{O1}$ paths in $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$. Activation energies for relaxed and compressed lattice parameters are shown as black and blue lines, respectively. Activation energies for the a -axis and c -axis relaxed cases are shown by red and green lines, respectively. Lattice parameters shown as blue lines are referenced ones [25]. The $\text{O1} \rightarrow \text{O3}$ path in oxygen migration and the atomic positions of strontium, iron, and oxygen atoms are given in section A-B. Purple arrows represent the movement of ions in oxygen migration.

extracted, and the oxidation state of Fe2 is $\text{Fe}^{4+}(d^4)$. The electronic structures in the oxygen migration are determined by the fourfold rotational symmetry around d orbitals and the orbital hybridization during the oxygen migration. In the case of the $\text{O1} \rightarrow \text{O3}$ path, the initial state has fourfold symmetry along the z axis and, therefore, the $d_{3z^2-r^2}$ state is fully occupied, while the $d_{x^2-y^2}$ state is empty because of the oxygen vacancy at the O3 site. As oxygen moves from the O1 site to the O3 site, the $d_{3z^2-r^2}$ state gradually moves up from occupied state to the empty state, while $d_{x^2-y^2}$ state gradually moves down from empty state to occupied state, keeping the band gap open. The final state does not have fourfold symmetry along the z axis and, therefore, the $d_{3z^2-r^2}$ state and the $d_{x^2-y^2}$ state are located both in the occupied and empty states. The electronic structure of the transition state is more similar to

that in the final state than the initial state because the atomic structure in the transition state is closer to that in the final state compared with the initial state.

In the case of the $\text{O2} \rightarrow \text{O1}$ path in $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$, the initial state does not have the fourfold symmetry along the z axis; therefore, the $d_{3z^2-r^2}$ state and the $d_{x^2-y^2}$ state are located both in the occupied and empty states. As oxygen moves from the O2 site to the O1 site, the $d_{3z^2-r^2}$ state gradually moves down from empty state to filled state, while the $d_{x^2-y^2}$ state gradually moves up from filled state to empty state. The final state has the fourfold symmetry along the z axis; therefore, the $d_{3z^2-r^2}$ state of the majority spin is fully occupied, and the $d_{x^2-y^2}$ state of majority spin is empty. However, in the case of minority spin, the $d_{3z^2-r^2}$ is located near the Fermi level; therefore, the electronic structure in $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$ is metallic. In the transition

FIG. 7. Activation energies of O1 $\rightarrow$ O3 and O2 $\rightarrow$ O1 paths in $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$ depending on the volume of the supercell. Solid and empty squares represent O1 $\rightarrow$ O3 and O2 $\rightarrow$ O1 paths, respectively.

state $d_{x^2-y^2}$ state exists across the Fermi level, leading to the metallic nature of the electronic structure in $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$.

2. $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$

We also investigated oxygen migration processes along the O1 $\rightarrow$ O3 and O2 $\rightarrow$ O1 paths. The initial states of both O1 $\rightarrow$ O3 and O2 $\rightarrow$ O1 migrations correspond to the structure of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ (X) in Fig. 1, while the final states of the O1 $\rightarrow$ O3 and O2 $\rightarrow$ O1 paths are represented by the structures of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ (Z) and $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ (Y), respectively in Fig. 1. The obtained activation energies for $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ are 1.00 and 1.16 eV for the O1 $\rightarrow$ O3 and O2 $\rightarrow$ O1 paths, respectively. It was confirmed that the oxygen diffusion paths and their activation barriers for $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ are similar to those for $\text{Sr}_3\text{Fe}_2\text{O}_{6.0-7.0}$. As for these paths, the atomic and electronic structures in the transition states are more similar to those in the final states than to those in the initial states. This trend is similar to the case of $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$.

In the case of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$, the electronic structures including the O1 $\rightarrow$ O3 path are insulating through the oxygen migration, while those of O2 $\rightarrow$ O1 are metallic near the transition state, and that finding is the same as that in the case of $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$. As oxygen moves from the O1 to O3 sites along the O1 $\rightarrow$ O3 path, the $d_{x^2-y^2}$ state in the minority spin is kept below the Fermi level, and the d_{yz} state in the minority spin moves up from the occupied state to the empty state, while d_{xy} state moves down from the empty state to the occupied state (see Fig. 8, lower left panel, and Fig. S4, left panel, in the Supplemental Material [53]).

In the case of the O2 $\rightarrow$ O1 path in $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$, as oxygen migrates from the O2 site to the O1 site, the d_{yz} and the $d_{x^2-y^2}$ states in the minority spin move up from the filled state to above the Fermi level, while the $d_{3z^2-r^2}$ state moves down from the empty state to below the Fermi level (see Fig. 8, lower right panel, and Fig. S4, right panel, in the Supplemental Material [53]). A more detailed description of the electronic structure in $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$ and $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ is provided in the Supplemental Material [53].

In the case of oxygen migration in $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$, O1 sites are almost fully occupied in the most stable structure; therefore O1 $\rightarrow$ O3 diffusion process should dominate, followed

FIG. 8. Structures of oxygen migration, activation energies, and partial densities of states of iron atoms for O1 $\rightarrow$ O3 and O2 $\rightarrow$ O1 paths in $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$ and $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$, respectively. Partial densities of states of Fe1 and Fe2 sites in the atomic structure are represented. Three partial densities of states are shown for initial, transition, and final states along the migration paths.

by O3 $\rightarrow$ O1 diffusion from another O3 site. The O2 $\rightarrow$ O1 path is available only if oxygen vacancies exist at O1 sites. Therefore, in the case of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$, where oxygen vacancies are located both at O1 and O3 sites, the migration path of O2 $\rightarrow$ O1 is as likely to occur as the O1 $\rightarrow$ O3 path.

IV. CONCLUSION

The mechanistic analysis of the oxygen transfer in the atomic-scale structure plays an important role in the development of various applications, such as the three-way catalysts for treating NO_x in automotive exhaust and solid-oxide fuel-cell electrolytes. The $n = 2$ Ruddlesden-Popper phases $\text{Sr}_3\text{Fe}_2\text{O}_{7.0-\delta}$ shows improved oxygen storage capacity, compared with the conventional material. In this paper, atomic structure, magnetic ordering, charged defects arising due to oxygen vacancies, and effect of lattice parameters on the ionic transport in $\text{Sr}_3\text{Fe}_2\text{O}_{5.75-7.0}$ were investigated by using DFT+ U calculations.

The investigation of the atomic structure and spin configurations in the case of $\text{Sr}_3\text{Fe}_2\text{O}_{5.75}$ revealed that the structure in

which all the O3 sites between the bilayers of FeO₆ octahedra are empty and the equatorial O1 sites of the FeO₆ octahedron are partially filled was found to be the most stable. Antiferromagnetic ordering in the planar and perpendicular directions is exhibited for the spin configuration of Sr₃Fe₂O_{5.75}. The calculated oxidation reaction energy for Sr₃Fe₂O_{6.0–7.0} was confirmed to be significantly small, i.e., below 0.1 eV. Relative formation energy of an oxygen defect between positive and neutral charge states in the case of Sr₃Fe₂O_{5.75–6.0} was examined. A singly positively charged defect was found to be stable at the position of ε_F from 0 to 1.12 eV above the valence band top ε_v . The neutral state is the most stable in the range of ε_F over 1.12 eV. We investigated the activation energies of oxygen diffusion using the equilibrium and compressively strained lattice parameters for Sr₃Fe₂O_{6.5}. The activation energies were found to be nearly proportional to the volume of the unit cell; namely, as the volume of the unit cell increases, the activation energy decreases. It was also found that in the oxygen-diffusion process, the activation energy of oxygen ion increases as the bond length between iron and oxygen decreases, and the bond length is minimum in the transition state, indicating that the iron oxygen repulsive interaction is the origin of the activation energy. In the compressed unit cell, the bond length of iron and oxygen ions is further shortened, giving rise to the higher activation energies. Calculated activation energies of oxygen ionic transport in Sr₃Fe₂O_{7.0–8}

with the oxygen content of 6.5 are 0.92 eV and 0.91 eV for the O1 → O3 path and the O2 → O1 path, respectively. And the obtained activation energies of Sr₃Fe₂O_{5.75} are 1.00 eV and 1.16 eV for the O1 → O3 path and the O2 → O1 path, respectively. O1 sites are almost fully occupied in the case of Sr₃Fe₂O_{6.5}; therefore, the O1 → O3 path should be dominant under the assumption of the O3 → O1 migration from another O3 site. On the contrary, the O1 sites in Sr₃Fe₂O_{5.75} are partially vacant in the most stable structure, indicating that the O2 → O1 path is a plausible migration path like the O1 → O3 path in Sr₃Fe₂O_{5.75}. As for the electronic structure of Sr₃Fe₂O_{6.5} and Sr₃Fe₂O_{5.75}, the electronic structure of the O1 → O3 path has an energy gap, while that of the O2 → O1 path is metallic near the transition state.

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