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 Oxygen Vacancy Formation and Ion Migration Mechanism in Layered Perovskite (Sr, La)₃Fe₂O_{7-δ}
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Abstract

Metal oxides are widely used in devices such as sensors, fuel cells, and oxygen permeation membranes. Understanding the oxide ion migration mechanism would provide fundamental insights into the relationships between structure and properties such as ionic conductivity. The Ruddlesden-Popper perovskite (Sr, La)_{*n*+1}(Fe, Co)_{*n*}O_{3*n*+1} (*n* = 2) has characteristic oxygen permeation and ion conduction properties, resulting from the layered perovskite structure. To elucidate the ion migration mechanism in Sr_{2.46}La_{0.54}Fe₂O_{7- σ} (SLF) we used a combination of experimental techniques [X-ray powder diffraction (XRPD) and enthalpy investigations of the oxygen vacancy formation reaction] and computational techniques [the bond valence sum (BVS) approach and *ab initio* density functional theory (DFT)]. The structural analyses of SLF by XRPD and DFT agreed well. They showed that the oxygen vacancies in SLF are located at the O1 oxygen site, which is on the vertex shared by two FeO₆ octahedra in the perovskite layer. Enthalpy of the oxygen vacancy formation changed at 830 °C. This is similar to the ionic conduction behavior reported for Sr₃Fe₂O₇. The XRPD study indicates that the host structural framework did not change with temperature, while the oxygen/vacancy arrangement in SLF did change at 830 °C. The BVS and DFT studies suggested a change in the ion migration pathway, in which the ion migration through O1 sites becomes more important at temperatures higher than 830 °C.

Introduction

Perovskite oxides (Sr, La)(Fe Co)O_{3- δ} are typical mixed conductive oxides, which may be suitable as cathodes for solid oxide fuel cells (SOFCs) or oxygen separators for partial oxidation reforming. However, the oxide ion conductivity for mixed conductive cubic or rhombohedral perovskites decreases abruptly as the temperature decreases. This reduces the performance of perovskite cathodes and oxygen separators at lower temperatures. To maintain the ion conductivity at lower temperatures, we have focused on the effect of crystal structure on ion conductivity. In particular, we have investigated (Sr, La)₃(Fe, Co)₂O_{7-δ}, which is composed of same elements as typical mixed conductive oxides of (Sr, La)(Fe Co)O_{3- δ}(LSCF).¹⁻³ (Sr, La)₃(Fe, Co)₂O_{7- δ} is a layered perovskite oxide that belongs to the Ruddlesden-Popper series, which is represented by the chemical formula $A_{n+1}B_nO_{3n+1}$ (n = 1, 2, 3, ...) where n = 2.⁴ It belongs to the space group *I4/mmm* (No. 139) (Fig. 1).⁵ The activation energies of oxygen permeability for the (Sr, La)_{n+1}(Fe, $Co)_n O_{3n+1}$ series are relatively lower than those of the typical mixed conductive perovskite $(Sr, La)(Fe, Co)O_{3-\delta}$ series.^{6,7} The lower activation energies result from the difference in the oxide ion migration mechanism of the cubic (or rhombohedral) and layered perovskites. The layered perovskite, (Sr, La)₃(Fe, Co)₂O_{7-δ}, possesses several different O ion transport pathways, in contrast to the single pathway in cubic perovskite oxides.⁷⁻¹⁰ Several migration pathways would lower the activation energy in the layered perovskite structure, allowing it to maintain a higher oxygen permeability and ion conductivity at lower temperatures. In this study, we investigate oxygen vacancy formation and oxide ion migration mechanism in layered perovskites from atomistic level viewpoint. $Sr_{2.46}La_{0.54}Fe_2O_{7-\delta}$ (SLF) was used, because of its relatively simple composition in the Sr3-xLaxFe2-yCoyO7-& series. In addition, SLF is chemically stable and exists as a single phase with no impurities. We examined the crystal structure and oxygen vacancy formation of SLF. In addition, we calculated the vacancy formation energies and ion migration energies by an *ab initio* density functional theory (DFT) calculations, and the possible ion migration trajectories by the bond valence sum (BVS) method. We discuss the ion migration mechanism in SLF based on the experimental and computational results.

Experimental procedures

Sample preparation

SLF ceramic samples were prepared by the conventional solid-state reaction method. La₂O₃ (99.9%), SrCO₃ (98%), and Fe₂O₃ (99.99%) powders were used as starting materials. La₂O₃ was initially heat-treated at 1000 °C for 8 h in air to remove moisture and CO₂ in the powder. The powders were weighed according to the composition of SLF and then ball-milled for 24 h using ZrO₂ balls and ethanol. After drying, the mixture was calcined at 1300 °C for 12 h in air. The calcined powders were ground and finally fired at 1420 °C for 12 h in air.

Sample characterization

The crystalline phase and crystal structure was characterized by X-ray powder diffraction (XRPD) using Cu $K\alpha_1$ radiation (1.54059 Å), selected with a Ge monochromator (X'pert MPD Pro, PANalytical Inc.). The X-rays were generated at 45 kV and 40 mA. The XRPD data were collected in air from room temperature (rt) to 900 °C using an electric furnace. 2θ step size for scanning was 0.017°. The data were refined by the Rietveld method using Rietan-FP.¹¹ The background in the XRPD pattern was refined by a finite sum of the Legendre polynomials.¹¹

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The oxygen defect content, δ , of SLF was evaluated by iodine titration at room temperature.¹² Powdered SLF was dissolved in 10 mass % KI aqueous solution and 12 M HCl. After 20 min, the reacted iodine was titrated with a 0.05 mol/L sodium thiosulfate standard solution until a colorless solution was obtained. Near the end-point, a small amount of starch solution was added to enhance the color change. The average Fe valence of SLF was estimated from the amount of titrated sodium thiosulfate, where the valences of the Sr and La ions were 3+ and 2+, respectively. δ was obtained from the average Fe valence calculated.

The temperature dependence of δ was investigated by thermogravimetric analysis (TGA). The SLF powder was weighed and placed in an electric furnace. The temperature was increased in stages up to 1200 °C under an air flow of 100 mL/min. The temperature dependence of the weight change was measured by a microbalance (DTG60/60H; Shimadzu); the weight change resulted from oxygen defect formation during heating.

Calculation of reduction reaction enthalpies ΔH

To examine the temperature dependence of oxygen vacancy formation in SLF, the reduction reaction enthalpies, ΔH , were calculated based on literature.^{8, 10, 13} The reduction reaction for SLF is described by Kröger-Vink notation as

$$Oo^{\times} + 2Fe_{Fe} \cdot (Fe^{4+}) = 1/2O_2 + Vo^{**} + 2Fe_{Fe}^{\times}(Fe^{3+}).$$
 (1)

By applying the law of mass action, eq. (1) can be written as

$$K = \frac{[\text{Vo}^{\bullet\bullet}]}{[\text{Oo}^{\star}]} \left(\frac{[\text{Fe}^{\star}]}{[\text{Fe}^{\bullet}]}\right)^2 Po_2^{1/2}$$
(2)

where K is the equilibrium constant for reaction (1). The composition of the SLF series is

 $(\mathrm{Sr}_{n+1-x}\mathrm{La}_x)(\mathrm{Fe}^{4+}_{n-x-2\delta}\mathrm{Fe}^{3+}_{x+2\delta})\mathrm{O}_{3n+1-\delta}$. Thus, eq. (2) is represented as

$$K = \frac{\delta}{3n+1-\delta} \left(\frac{x+2\delta}{n-x-2\delta}\right)^2 Po_2^{1/2} = K' \exp\left(-\frac{\Delta H}{kT}\right)$$
(3)

where *K*' is related to the reduction reaction entropy, ΔS ; *k* is the Boltzmann constant; and n = 2 for SLF. The temperature dependence of *K* is calculated from the δ values obtained from TGA. ΔH is determined from the slope of the Arrhenius plot of *K*. The *K*' was assumed as temperature independence. Note that temperature change in disordering of the lattice or of the randomized vacancies is possibly disregarded, because no structural phase transition is present in the SLF.

Oxide ion-accessible pathways by the bond valence sum method

Possible oxide ion migration pathways at 400 and 900 °C were estimated by using the BVS method.¹⁴⁻¹⁷ In this method, it is assumed that the BVS of the mobile oxide ions matches the nominal charge (-2) for the equilibrium sites and any sites that an ion accesses along its pathway. This straightforwardly leads to model pathways by the set of "accessible" sites in the structure corresponding to a BVS mismatch, between calculated and ideal values, lower than a threshold value $|\Delta V(O)|$. Calculations were performed in a unit cell with a mesh of 200³ grid points using our computer program for the structural parameters obtained from the Rietveld refinements at 400 and 900 °C. The 3D visualizations were created with the marching cubes algorithm.¹⁸

Ab initio DFT calculations of oxygen vacancy formation energies and vacancy migration energies

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To estimate oxygen vacancy formation energies and vacancy migration energies for SLF, *ab initio* DFT calculations were conducted using the Vienna Ab Initio Simulation Package $(VASP)^{19,20}$ with a modified Perdew-Burke-Ernzerhof generalized gradient approximation (PBEsol-GGA)^{21,22} and the projector-augmented wave (PAW) method.²³ The on-site Coulomb correction (GGA + *U*) was included for localized electronic states, and the *U* value was 5 eV for Fe 3*d* states, according to literature values.^{24, 25}

Results and discussion

X-ray structure refinement

Figures 2 and 3 show the XRPD patterns of the SLF sample at room temperature, 400, 500, 600, 700, 800, and 900 °C, where number of reflections was 127 in the 2θ range from 10° to 151°. The XRPD patterns of the SLF samples confirmed the formation of the Ruddlesden-Popper layered perovskite structure for Sr₃Fe₂O₇ (*I4/mmm*, *Z* = 2) at each temperature. No secondary phases were observed. The refined structural parameters at each temperature are presented in Table 1. Because the occupancy and the displacement parameters for oxide ions are interrelated, the occupancy was determined before the displacement parameter. The total occupancy of the oxide ions was fixed based on the total oxygen content, 7- δ , which was estimated by iodine titration and TGA. If the occupancy of any oxide sites exceeded unity upon Rietveld refinement, it was fixed at unity.

From the lattice parameters refined by the Rietveld analysis, the linear thermal expansion coefficient was estimated to be 18.8×10^{-6} K⁻¹ for the a(b)-axis and 16.0×10^{-6} K⁻¹ for the *c*-axis from room temperature to 900 °C. No structural phase transition was observed in this temperature range. The La ions occupied the 2a sites in preference to the 4e sites in the I4/mmm space group.

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The Fe-O bond lengths estimated from the refined structural parameters are shown in Table 2. For the Fe-O1 or Fe-O3 bonds, the bond lengths were larger at higher temperatures. However, the Fe-O2 bond length remained almost constant from 400 to 900 °C. Thus, the FeO₆ octahedron became more asymmetric as temperature was increased.

Oxygen vacancy formation

The oxygen content of 7- δ at room temperature was determined as 7.00(2) by the titration method, indicating that there were no significant oxygen vacancies. Figure 4 shows the temperature dependence of 7- δ , refined by the iodine titration and TGA results. Above 400 °C, 7- δ gradually decreased with increasing temperature. The Rietveld analysis showed that with increasing temperature, the occupancy at only the O1 site decreased with the δ value. However, a small number of oxygen vacancies at the O3 site were observed at 900 °C, indicating that the vacancy formation and distribution were different at higher temperatures.

Based on the oxygen vacancy content, δ , an Arrhenius plot of the equilibrium constant, *K*, is shown in Fig. 5. The slope of the plot changed considerably at a critical temperature of ~830 °C, indicating two values of the vacancy formation enthalpy, ΔH , between 400 and 1200 °C. ΔH was calculated as 1.0(1) eV at temperatures below ~830 °C, whereas it was 2.0(1) eV at temperatures above the critical temperature. Therefore, the oxygen vacancy formation changes at temperatures above ~830 °C. A similar trend has been reported in the Arrhenius plot of the ion conductivity for Sr₃Fe₂O_{7- δ}⁸ in which the activation energies were 1.3 and 2.3 eV in the lower and higher temperature regions, respectively. This implies that the change in conductivity at 830 °C is related to the

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formation and distribution of vacancies in the lattice, because no structural phase transition was observed by XRPD at the temperature.

The oxygen vacancy formation energies were estimated by DFT calculation. A superstructure consisting of four unit cells ($2 \times 2 \times 1$) was used to reproduce Sr and La distribution (Fig. 6). The lattice parameters and fractional coordinates were relaxed for the non-vacant structure at the oxygen sites; the formula unit of the cell corresponded to Sr₂₂La₂Fe₁₆O₅₆. To simplify the structure based on the Rietveld refinement, we assumed that all the cation sites in the rock-salt slab were occupied by Sr ions, whereas the A-sites of the perovskite slab were composed of La and Sr ions in a 1: 3 ratio. The final energies of the optimized structural geometries were recalculated to correct for changes in the plane-wave basis during relaxation. A kinetic energy cutoff of 500 eV and a Monkhorst-Pack $2 \times 2 \times 1$ k-points mesh were set, which led to energy convergence within 5 meV / atom. The tetragonal lattice parameters calculated for the original unit cell were (*a*, *c*) = (3.8386, 20.0876) Å, which were comparable to our experimental results, (*a*, *c*) = (3.87762(3), 20.2102(2)) Å, which was within the typical error for the GGA.

The oxygen vacancy formation energies, E_{vac} , can be expressed as

$$E_{\rm vac} = E({\rm Sr}_{22}{\rm La}_2{\rm Fe}_{16}{\rm O}_{55}) + 1/2 \ E({\rm O}_2) - E({\rm Sr}_{22}{\rm La}_2{\rm Fe}_{16}{\rm O}_{56}) \tag{4}$$

where E(X) is the total electron energy of composition *X*. The calculated oxygen vacancy formation energies correspond to the experimental enthalpies, if the pressure and volume term, *PV*, and the entropy contribution are neglected. Although the XRPD results indicated three crystallographic O sites, we obtained four vacancy formation energies, because the ordered arrangement of La/Sr in our superstructure model split the O3 site into two symmetrically distinct oxygen sites, O3-1 and O3-2 (Fig. 6(b)). The O3-1 site was coordinated to one La and three Sr ions in neighboring perovskite A-sites, whereas there were no neighboring La ions for the O3-2 site. For computations of the O-deficient cells, we fixed the lattice constants using tetragonal lattice parameters of non-vacancy composition, hereinafter, unless specially mentioned. Note that applying full structure relaxation for the O-deficient cells showed small deviation of less than 0.7 % and 35 meV for cell volume and total energy, respectively.

Table 3 (second column) compares the oxygen vacancy formation energies of the four distinct crystallographic sites. The total energy of isolated O_2 molecule, $E(O_2)$, was estimated under the periodic boundary condition using 20 Å cubic-cell with gamma-point sampling. However, the estimated vacancy formation energy using eqn.(4) does not take into account any difference owning to an over-binding of the GGA in the O_2 molecule.²⁶ To compare the oxygen vacancy formation energies of the four oxide ion sites, we treated the $E(O_2)$ term as constant and calculated the energy difference between the oxygen vacancy phase and the corresponding non-vacant phase. The lowest, most stable, oxygen vacancy formation energy was set as zero for comparison, and listed also in third column of Table 3. The results indicate that the oxygen vacancy formation energies were mainly between 0 and 1.00 eV for the four sites.

 La)FeO_{3- δ}.

We also employed the Bader charge analysis²⁹⁻³¹ for the ions before and after oxygen vacancy formation. The valence state of Fe ions is around +1.95 for non-vacant SLF, and slightly reduces to around +1.85. Charge disproportion at Fe ions were not indicated for both the SLFs with and without O vacancy. The valence state of O1 site (-1.16) is slightly smaller than the other oxygen sites (-1.25) in SLF. This may be related to the smaller vacancy formation energy at the O1 sites. We intended to elucidate the relationship between vacancy formation and electronic structure in future.

Oxide ion migration mechanism

Figure 7(a) and (b) shows the oxide ion migration pathways estimated with the BVS method using the refined structural parameters at 400 and 900 °C. In both cases, the isosurfaces corresponded to BVS mismatch thresholds of $|\Delta V(O)| = 0.12$. A continuous 2D pathway located mainly in the rock-salt layer was observed. This pathway linked the O2 oxide ions in a complex nonlinear indirect way. The O2 site positions were shifted with respect to this pathway, indicating a mismatch between the actual BVS value at the O2 site and the ideal one. In addition, the DFT calculations showed that the vacancy formation energy was larger at the O2 sites (Table 3), meaning that oxide ion migration along the O2-O2 pathway was unlikely. The present BVS method cannot account for oxygen vacancy formation, and only predicts sites accessible to oxide ions. It appears that at 400 °C (Fig. 7(a)), only isolated isosurfaces around O1 and O3 site were obtained in the perovskite layer with a threshold. However, increasing the threshold value to $|\Delta V(O)| = 0.52$ (not shown) was sufficient to connect the O1-O3, O3-O3, and O3-O2 sites, thus these three paths are possible migration paths. More interestingly, the pathway O1 \rightarrow O3 \rightarrow O1

 \rightarrow O3 (Path 1) was completely continuous at 900 °C (Fig. 7(b)), whereas it was not at 400 °C for the same threshold criteria. This indicates that Path 1 becomes more important for oxide ion migration at higher temperatures.

To evaluate the migration energy, which is the energy barrier for oxygen vacancy hopping in SLF, the nudged elastic band (NEB) approach³² was used to identify plausible vacancy hopping between the O1, O2, and O3 sites. Typical energy profiles for oxide ion migration are presented in Fig. 8. (O1 \rightarrow O3-1 site) The energy maximum was midway between the two oxygen sites; therefore, the migration energy of the oxide ion was defined as the energy difference between the energy maximum and the local minima where the oxide ion was located at the O1 or O3-1 site. Bader charge analysis for neighboring and surrounding Fe ions indicated small electron transfer during migration process. In particular, oxygen vacancy migration between O1 and O3 sites accompanies the change of Bader charges at neighboring Fe sites around 0.25. This would be related to the smaller charge in the O1 sites than the other sites as mentioned above. However, no distinct charge disproportion, *i.e.* formation of polaron, was seen in the present study. Therefore, we disregarded the polaron assisted oxide migration mechanism as indicated in the previous study.³³

The migration energies of the oxide ions and oxygen vacancies are symmetrical around the hopping routes in the energy profiles. Thus, the hopping routes and the corresponding migration energies of the oxygen vacancy between possible oxygen sites calculated using this symmetry are listed in Table 4. The hopping route for O1 \rightarrow O3 (Path 1) and O2 \rightarrow O3 (Path 2) had asymmetric migration energies, because of the difference in vacancy formation energies between the O1, O2, and O3 sites. The larger migration energy in the asymmetric profile corresponded to the rate-determining process for each path. The

migration energies of the O3 \rightarrow O3 path (Path 3), except for the O3-1 \rightarrow O3-1 jump, tended to be slightly smaller (~0.7 eV) than those of Path 1 (~1.0 eV) and Path 2 (~0.9 eV). The direct pathway between O2 sites (Path 4) showed a much higher migration energy (1.8 eV) than Paths 1-3. Thus, the oxygen vacancies (oxide ions) mainly migrated through Path 3, although the vacancy concentrations at the O3 sites were much smaller than at the O1 sites (Table 1 or 3). Based on these results, the ion migration along Paths 1, 2, and 3 contributes to the ion conductivity in SLF. In addition, we propose that the change in the reported activation energy for the ion conductivity stems from the slight difference in the migration energies between Path 3 and Paths 1 and 2. In other words, Path 3 contributes to the ion migration at all temperatures, whereas the oxide ions jump via Paths 1 and 2 at higher temperatures. The activation energies, E_{a} , for the ion conductivity are composed of two contributions: the migration energy, E_m , and ΔH of the reduction reaction according to reaction (3), as follows:

$$E_{\rm a} = \Delta H/2 + E_m \tag{5}$$

If $E_{\rm m}$ is 0.7 eV, which corresponds to the migration energy through Path 3, $E_{\rm a}$ was estimated as 1.2 and 1.7 eV for the lower and higher temperature regions, using the ΔH values obtained from Fig. 5. The difference in $E_{\rm a}$ between the lower and higher temperatures was smaller than that of the reported ion conductivity. This suggests that $E_{\rm m}$ also increased at higher temperatures because of additional oxide ions jumping via Paths 1 and 2.

To sum up, we propose the following ion migration mechanism. The ion migration through Path 3 plays a major role in the ion conductivity at temperatures lower than 830 °C. However, at higher temperatures, the mechanism is slightly different, in that Paths 1 and 2 also contribute to oxide ion migration. In particular, the greater number of

oxygen vacancies at the O1 sites would encourage ion conductivity, arising from the ion migration from O3 sites to neighboring O1 sites.

If we compare the layered SLF with cubic or rhombohedral (Sr, La)FeO_{3- δ} series, ^{27,28} the migration energies through the Path 3 is similar to that of the (Sr, La)FeO_{3- δ}. However, migration energies through the O1 sites are larger than those of the (Sr, La)FeO_{3- δ}. For the (Sr, La)FeO_{3- δ}, presence of La encourages the migration.^{27,28} In the case of layered SLF, the results of the Table 4 suppose that the La doping is effective to encourage the migration through the Path 3, while it prevents the migration thorough the Path 1.

Conclusion

A Ruddlesden-Popper layered perovskite structure of $Sr_{n+1}Fe_nO_{3n+1}$ (n = 2) was observed for SLF from room temperature to 900 °C. No other secondary phases were observed. The Rietveld analysis showed that the structure was well refined based on the space group *I4/mmm*. Oxygen vacancies were created at the O1 sites, in preference to the O2 or O3 sites. In the Arrhenius plot of the equilibrium constant, *K*, for the reduction reaction, the slope changed remarkably at approximately 830 °C, suggesting a change in oxygen vacancy formation and arrangement. Indeed, some oxygen vacancies were created at the O3 sites at 900 °C, whereas no oxygen vacancies were present at the O3 sites below 800 °C upon the Rietveld refinement. The BVS and DFT studies suggested that the ion conductivity behavior stems from a change in the ion migration and the oxygen/vacancy arrangement. The ion migration through Path 3 plays a main role in ion conductivity at temperatures lower than 830 °C. However, at higher temperatures, Paths 1 and 2 additionally contribute to the ion migration, resulting in variation of ion conductivity.

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Figure captions

Fig. 1 Crystal structure of layered perovskite (Sr, La)₃Fe₂O_{7-δ}.

Fig. 2 XRPD patterns at room temperature, 400, 500, and 600 °C and fitting profiles from the Rietveld analysis.

Fig. 3 XRPD patterns at 700, 800, and 900 °C and fitting profiles from the Rietveld analysis.

Fig. 4 Temperature dependence of oxygen content 7- δ .

Fig. 5 Arrhenius plot of the equilibrium constant, K, for SLF4310. Solid line is the fit of eq.

(3).

Fig. 6 (a) Superstructure of the formula unit corresponding to $Sr_{22}La_2Fe_{16}O_{56}$ for the DFT

calculation. (b) Magnification of the FeO₆ octahedron in (a) and a plausible hopping path.

Fig. 7 Oxide ion-accessible pathways at 400 and 900 °C estimated from the BVS method.

Fig. 8 Energy profiles of vacancy hopping between O1 and O3.

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Table captions

Table 1 Structural parameters and oxygen vacancy concentration δ at room temperature,

400, 500, 600, 700, 800, and 900 °C refined by the Rietveld analysis. M is formula weight.

Sr1/La1, Fe, O2 atoms are at 4e (0, 0, z) positions; Sr2/La2 at 2a (0, 0, 0); O1 at 2b (0, 0,

0.5); O3 at 8g (0, 0.5, z) positions.

Table 2 Bond lengths (Å) of Fe-O at each temperature.

Table 3 Oxygen vacancy formation energies of each O site.

Table 4 Migration energies for the possible oxide ion migration.



Fig. 1





Fig. 2

254x190mm (96 x 96 DPI)



Fig. 3

254x190mm (96 x 96 DPI)





Fig. 4

254x190mm (96 x 96 DPI)



Fig. 5

254x190mm (96 x 96 DPI)









Fig. 7



Fig. 8

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Table 1 Structural parameters and oxygen vacancy concentration δ at room temperature, 400, 500, 600, 700, 800, and 900 °C refined by the Rietveld analysis. M is formula weight. Sr1/La1, Fe, O2 atoms are at 4e(0, 0, z)positions; Sr2/La2 at 2a (0, 0, 0); O1 at 2b (0, 0, 0.5); O3 at 8g (0, 0.5, z) positions.

Temp /°C		rt	400	500	600	700	800	900
Temp. / C		It	400	500	000	700	800	900
М		514 24	514 24	513 30	511 38	510.10	508 50	506 52
a b/Å		3.87762(3)	3.89243(3)	3.89879(2)	3.90758(2)	3.91937(2)	3.93012(2)	3.94156(2)
c/Å		20.2102(2)	20.3558(2)	20.3609(2)	20.3790(2)	20.4121(2)	20.4479(2)	20.4927(2)
0 /11		20.2102(2)	2010000(2)	2010 000 (2)	2010 / 20(2)		(_)	(_)
δ		0.00(2)	-0.01(2)	0.06(2)	0.18(2)	0.26(2)	0.36(2)	0.49(2)
Sr1	Occupancy	0.91(1)	0.90(1)	0.90	0.90	0.90	0.90	0.90
	z	0.1833(1)	0.1839(1)	0.1838(1)	0.1836(1)	0.1837(1)	0.1836(1)	0.1837(1)
	$U_{\rm iso} \ge 10^2 / {\rm \AA}^2$	0.66(2)	1.09(4)	1.10(2)	1.47(4)	1.63(3)	1.91(4)	2.00(4)
		0100(_)		(_)				
La1	Occupancy	0.09(1)	0.10(1)	0.10	0.10	0.10	0.10	0.10
	z	0.1833(1)	0.1839(1)	0.1838(1)	0.1836(1)	0.1837(1)	0.1836(1)	0.1837(1)
	$U_{\rm iso} \times 10^2 / {\rm \AA}^2$	0.66(2)	1.09(4)	1.10(2)	1.47(4)	1.63(3)	1.91(4)	2.00(4)
	100							
Sr2	Occupancy	0.64(1)	0.66(1)	0.66	0.66	0.66	0.66	0.66
	$U_{\rm iso} \times 10^2 / {\rm \AA}^2$	0.7(4)	1.09(5)	1.29(5)	1.41(5)	1.75(5)	1.83(5)	2.03(5)
La2	Occupancy	0.36(1)	0.34(1)	0.34	0.34	0.34	0.34	0.34
	$U_{\rm iso} \ge 10^2/{\rm \AA}^2$	0.7(4)	1.09(5)	1.29(5)	1.41(5)	1.75(5)	1.83(5)	2.03(5)
Fe	Occupancy	1	1	1	1	1	1	1
	z	0.4003(1)	0.4019(1)	0.4011(1)	0.4006(1)	0.4002(1)	0.3993(1)	0.3989(1)
	$U_{\rm iso} \ge 10^2$ /Å ²	0.21(3)	0.65(4)	0.52(4)	0.59(4)	0.75(4)	0.76(4)	0.80(4)
O1	Occupancy	1	1	0.94(3)	0.86(3)	0.74	0.64	0.58(2)
	$U_{\rm iso} \ge 10^2$ /Å ²	3.5(5)	2.4(5)	4.3(6)	1.3(5)	5.1(8)	5.1(9)	5.0(10)
O2	Occupancy	1	1	1.00(3)	0.98(3)	1	1	1
	z	0.3065(3)	0.3075(4)	0.3064(4)	0.3056(4)	0.3049(5)	0.3058(4)	0.3048(4)
	$U_{\rm iso} \ge 10^2$ /Å ²	0.3(3)	1.3(2)	1.3(1)	1.6(3)	1.7(2)	1.2(2)	1.3(2)
02	Occurrency	1	1	1	1	1	1	0.084(4)
03	occupancy	0.0027(2)	0.0041(4)	0.0040(4)	0.0016(4)	0.0017(4)	0.0023(4)	0.984(4)
	χ $10^2/\lambda^2$	0.0927(3)	0.0941(4)	0.0940(4)	0.0910(4)	0.0917(4)	0.0923(4)	0.0908(4)
	$U_{\rm iso}$ x 10 /A	0.9(1)	0.8(1)	1.4(1)	1.4(1)	1.9(1)	2.3(1)	2.2(2)
$R_{\rm wp}$		3.37	3.75	3.65	3.72	3.43	3.4	3.35
$R_{\rm p}$		2.53	2.88	2.81	2.87	2.64	2.62	2.58
S		1.21	1.13	1.13	1.12	1.13	1.14	1.13

Temp. /°C	rt	400	500	600	700	800	900
Fe-O1 /Å	2.014(2)	1.997(2)	2.014(2)	2.026(2)	2.037(2)	2.059(2)	2.072(2)
Fe-O2 /Å	1.896(6)	1.922(8)	1.928(8)	1.936(8)	1.945(10)	1.912(8)	1.928(8)
Fe-O3 /Å	(x4) 1.9440(5)	1.9479(4)	1.9520(4)	1.9603(7)	1.9667(7)	1.9737(8)	1.9821(9)

Table 2 Bond lengths (Å) of Fe-O at each temperature.

Site	Oxygen vacancy	Oxygen vacancy
	formation energy (Eqn.4)	formation energy
	/eV	(Relative) /eV
01	0.72	0.00
O2	1.72	1.00
O3-1	1.28	0.55
O3-2	1.39	0.67

Table 3 The oxygen vacancy formation energies of each O site according to Eqn.4. Relative energy was obtained by setting the most stable energy as zero. (See main text)

Reference	Jump route	Oxygen vacancy migration energy /eV	 Table 4 Migration energies for the possible oxide ion migration
Path 1 (O1 - O3)	01 → 03-1	0.87	
	03-1 → 01	0.30	
	01 → 03-2	1.05	
	O3-2 → O1	0.39	
Path 2 (O2 - O3)	O2 → O3-1	0.46	
	O3-1 → O2	0.91	
	O2 → O3-2	0.52	
	O3-2 → O2	0.85	
Path 3 (O3 - O3)	O3-1 → O3-1	0.85	
	03-1 → 03-2	0.71	
	O3-2 → O3-2	0.67	
Path 4 (O2 – O2)	O2 → O2	1.81	