Supplementary Information

High oxide-ion conductivity by the overbonded channel oxygens in Si-deficient $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$ apatite without interstitial oxygens

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(A) Results of the structure analysis of the single crystal time-of-flight neutron-diffraction data of $La_{9.333}Si_6O_{26}$ and $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$. Details of single-crystal X-ray diffraction experiments of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$.

Table S1. Atomic Coordinates and Atomic Displacement Parameters Refined Using the Single-Crystal Neutron-Diffraction Data of $La_{9.333}Si_6O_{26}$, Based on the Structure Model with O3 and O4 Non-Split Sites and without Interstitial Oxygens.

Site	Wyckoff position	*g*	*x*	*y*	*z*	U_{eq} (Å^2)
La1	4*f*	0.8325	1/3	2/3	−0.0014(3)	0.0122(4)
La2	6*h*	1	0.01390(11)	0.24385(11)	1/4	0.0074(4)
Si	6*h*	1	0.4012(2)	0.3713(2)	1/4	0.0068(7)
O1	6*h*	1	0.3228(2)	0.4840(2)	1/4	0.0189(7)
O2	6*h*	1	0.59348(17)	0.47182(18)	1/4	0.0134(5)
O3	12*i*	1	0.34499(19)	0.25432(15)	0.06959(18)	0.0252(6)
O4	2*a*	1	0	0	1/4	0.0243(9)

Site	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)	U_{13} (Å^2)	U_{23} (Å^2)
La1	0.0054(5)	= U_{11}	0.0259(9)	= U_{11}/2	0	0
La2	0.0062(5)	0.0076(5)	0.0071(5)	0.0025(4)	0	0
Si	0.0062(8)	0.0087(8)	0.0062(9)	0.0041(7)	0	0
O1	0.0247(8)	0.0249(8)	0.0186(9)	0.0211(7)	0	0
O2	0.0070(7)	0.0100(7)	0.0188(8)	0.0010(5)	0	0
O3	0.0502(9)	0.0139(6)	0.0110(6)	0.0158(6)	−0.0148(5)	−0.0050(4)
O4	0.0114(8)	= U_{11}	0.050(2)	= U_{11}/2	0	0

g : Occupancy factor. U_{eq} : Equivalent isotropic atomic displacement parameter. U_{ij}: Anisotropic atomic displacement parameters. R_1 : 0.0759, wR_2 : 0.0967, $\Delta\rho_{max}$ / $\Delta\rho_{min}$: 0.60 / –0.64 fm Å^{-3}

Table S2 (Same as Table 2 in the main text). Atomic Coordinates and Atomic Displacement Parameters Refined Using the Single-Crystal Neutron-Diffraction Data of $La_{9.333}Si_6O_{26}$, Based on the Structure Model with O3a and O3b Split Sites, with O4 Non-Split Site and without Interstitial Oxygens (**Final Refinement of Neutron Data of $La_{9.333}Si_6O_{26}$**).

Site	Wyckoff position	*g*	*x*	*y*	*z*	U_{eq} (Å^2)	BVS
La1	4*f*	0.8325	1/3	2/3	–0.0012(2)	0.0126(4)	2.95
La2	6*h*	1	0.01378(10)	0.24380(10)	1/4	0.0076(4)	2.83
Si	6*h*	1	0.4013(2)	0.3713(2)	1/4	0.0066(6)	3.98
O1	6*h*	1	0.32295(19)	0.48410(19)	1/4	0.0190(6)	1.95
O2	6*h*	1	0.59363(16)	0.47196(16)	1/4	0.0135(5)	2.03
O3a	12*i*	0.82(2)	0.3512(8)	0.2557(2)	0.0668(4)	0.0134(11)	1.90
O4	2*a*	1	0	0	1/4	0.0251(8)	2.09
O3b	12*i*	0.18 = (1−*g*(O3a))	0.297(2)	0.2438(8)	0.0906(13)	U_{iso} 0.007(3)	1.99

Site	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)	U_{13} (Å^2)	U_{23} (Å^2)
La1	0.0062(4)	= U_{11}	0.0253(8)	= U_{11}/2	0	0
La2	0.0065(4)	0.0079(5)	0.0068(5)	0.0025(3)	0	0
Si	0.0063(8)	0.0071(8)	0.0063(8)	0.0033(6)	0	0
O1	0.0251(8)	0.0246(8)	0.0189(8)	0.0212(7)	0	0
O2	0.0067(6)	0.0101(6)	0.0190(7)	0.0006(5)	0	0
O3a	0.021(2)	0.0131(7)	0.0066(8)	0.0093(8)	-0.0043(9)	-0.0026(5)
O4	0.0122(8)	= U_{11}	0.051(2)	= U_{11}/2	0	0

BVS : Bond valence sum. R_1 : 0.0669, wR_2 : 0.0891, $\Delta\rho_{max}$ / $\Delta\rho_{min}$: 0.52 / −0.56 fm Å^{-3}

Table S3. Atomic Coordinates and Atomic Displacement Parameters Refined Using the Single-Crystal Neutron-Diffraction Data of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$, Based on the Si-Vacancy Model with O3 and O4 Non-Split Sites and without Interstitial Oxygens.

Site	Wyckoff position	*g*	*x*	*y*	*z*	U_{eq} (Å^2)
La1	4*f*	0.8912	1/3	2/3	–0.0011(2)	0.0121(4)
La2	6*h*	1	0.01213(11)	0.23940(11)	1/4	0.0095(4)
Si	6*h*	0.971	0.4032(2)	0.3729(2)	1/4	0.0052(7)
O1	6*h*	1	0.3251(2)	0.4862(2)	1/4	0.0186(7)
O2	6*h*	1	0.59581(16)	0.47289(16)	1/4	0.0141(6)
O3	12*i*	1	0.34826(17)	0.25701(14)	0.0686(2)	0.0247(6)
O4	2*a*	1	0	0	1/4	0.080(3)

Site	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)	U_{13} (Å^2)	U_{23} (Å^2)
La1	0.0083(4)	= U_{11}	0.0199(9)	= U_{11}/2	0	0
La2	0.0066(5)	0.0099(5)	0.0110(6)	0.0034(4)	0	0
Si	0.0053(8)	0.0057(8)	0.0057(12)	0.0035(7)	0	0
O1	0.0262(8)	0.0234(8)	0.0172(11)	0.0206(7)	0	0
O2	0.0076(6)	0.0101(7)	0.0210(10)	0.0018(5)	0	0
O3	0.0473(8)	0.0148(6)	0.0137(8)	0.0168(5)	–0.0156(5)	–0.0055(4)
O4	0.0119(10)	= U_{11}	0.217(8)	= U_{11}/2	0	0

R_1 : 0.0727, wR_2 : 0.1032, $\Delta\rho_{max}$ / $\Delta\rho_{min}$: 0.65 / –0.59 fm Å^{-3}

Table S4. Atomic Coordinates and Atomic Displacement Parameters Refined Using the Single-Crystal Neutron-Diffraction Data of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$, Based on the Si-Vacancy Model with O3a and O3b Split Sites, with O4 Non-Split Site and without Interstitial Oxygens.

Site	Wyckoff position	*g*	*x*	*y*	*z*	U_{eq} (Å^2)
La1	4*f*	0.8912	1/3	2/3	–0.0010(2)	0.0123(4)
La2	6*h*	1	0.01209(10)	0.23940(10)	1/4	0.0095(4)
Si	6*h*	0.971	0.40314(19)	0.37290(19)	1/4	0.0054(7)
O1	6*h*	1	0.32502(19)	0.48627(18)	1/4	0.0184(6)
O2	6*h*	1	0.59583(15)	0.47288(15)	1/4	0.0144(5)
O3a	12*i*	0.84(2)	0.3529(7)	0.2581(2)	0.0665(4)	0.0151(11)
O4	2*a*	1	0	0	1/4	0.078(3)
O3b	12*i*	0.16 =(1−*g*(O3a))	0.298(2)	0.2447(9)	0.0927(15)	U_{iso} 0.007(3)

Site	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)	U_{13} (Å^2)	U_{23} (Å^2)
La1	0.0085(4)	= U_{11}	0.0199(9)	= U_{11}/2	0	0
La2	0.0071(4)	0.0099(5)	0.0105(6)	0.0035(3)	0	0
Si	0.0050(8)	0.0062(8)	0.0060(11)	0.0036(6)	0	0
O1	0.0263(8)	0.0232(7)	0.0171(10)	0.0210(7)	0	0
O2	0.0078(6)	0.0101(6)	0.0218(9)	0.0019(5)	0	0
O3	0.024(2)	0.0140(7)	0.0092(9)	0.0111(8)	–0.0067(10)	–0.0037(5)
O4	0.0129(10)	= U_{11}	0.208(8)	= U_{11}/2	0	0

R_1 : 0.0624, wR_2 : 0.0968, $\Delta\rho_{max}$ / $\Delta\rho_{min}$: 0.78 / –0.61 fm Å^{-3}

Table S5. Atomic Coordinates and Atomic Displacement Parameters Refined Using the Single-Crystal Neutron-Diffraction Data of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$, Based on the Si-Vacancy Model with O3 Non-Split Site, with O4a and O4b Split Sites and without Interstitial Oxygens.

Site	Wyckoff position	*g*	*x*	*y*	*z*	U_{eq} (Å^2)
La1	4*f*	0.8912	1/3	2/3	–0.0011(2)	0.0124(4)
La2	6*h*	1	0.01213(11)	0.23936(11)	1/4	0.0094(4)
Si	6*h*	0.971	0.4032(2)	0.3729(2)	1/4	0.0052(7)
O1	6*h*	1	0.3250(2)	0.48611(19)	1/4	0.0186(7)
O2	6*h*	1	0.59575(16)	0.47293(16)	1/4	0.0142(6)
O3	12*i*	1	0.34812(17)	0.25692(14)	0.0685(2)	0.0248(5)
O4a = O4	2*a*	0.68(3)	0	0	1/4	0.031(4)
O4b	4*e*	0.16 =(1−*g*(O4a))/2	0	0	0.144(5)	=O4

Site	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)	U_{13} (Å^2)	U_{23} (Å^2)
La1	0.0083(4)	= U_{11}	0.0207(9)	= U_{11}/2	0	0
La2	0.0066(5)	0.0100(5)	0.0106(6)	0.0033(4)	0	0
Si	0.0054(8)	0.0059(8)	0.0058(11)	0.0038(7)	0	0
O1	0.0258(8)	0.0233(8)	0.0173(11)	0.0203(7)	0	0
O2	0.0078(6)	0.0104(7)	0.0212(10)	0.0021(5)	0	0
O3	0.0474(8)	0.0149(5)	0.0138(8)	0.0170(5)	–0.0155(5)	–0.0056(4)
O4a, O4b*	0.0108(11)	= U_{11}	0.071(12)	= U_{11}/2	0	0

* U_{ij}(O4a) = U_{ij}(O4b), R_1 : 0.0716, wR_2 : 0.1024, $\Delta\rho_{max}$ / $\Delta\rho_{min}$: 0.48 / –0.45 fm Å^{-3}

Table S6 (Same as Table 3 in the main text). Atomic Coordinates and Atomic Displacement Parameters Refined Using the Single-Crystal Neutron-Diffraction Data of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$, Based on the Si-Vacancy Model with O3a, O3b, O4a and with O4b Split Sites and without Interstitial Oxygens **(Final Refinement of Neutron Data of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$)**.

Site	Wyckoff position	*g*	*x*	*y*	*z*	U_{eq} (Å^2)
La1	4*f*	0.8912	1/3	2/3	−0.0010(2)	0.0127(4)
La2	6*h*	1	0.01213(10)	0.23936(10)	1/4	0.0095(4)
Si	6*h*	0.971	0.40316(19)	0.37291(19)	1/4	0.0054(7)
O1	6*h*	1	0.32493(18)	0.48610(18)	1/4	0.0184(6)
O2	6*h*	1	0.59574(15)	0.47295(15)	1/4	0.0144(5)
O3a	12*i*	0.84(2)	0.3528(7)	0.2581(2)	0.0665(4)	0.0150(11)
O4a = O4	2*a*	0.68(3)	0	0	1/4	0.032(4)
O3b	12*i*	0.16 =(1−*g*(O3a))	0.298(2)	0.2444(9)	0.0920(15)	U_{iso} 0.008(3)
O4b	4*e*	0.159 =(1−*g*(O4a)/2	0	0	0.144(5)	0.032(4)

Site	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)	U_{13} (Å^2)	U_{23} (Å^2)
La1	0.0087(4)	= U_{11}	0.0206(9)	= U_{11}/2	0	0
La2	0.0070(4)	0.0101(5)	0.0104(6)	0.0035(3)	0	0
Si	0.0052(8)	0.0062(7)	0.0061(11)	0.0039(6)	0	0
O1	0.0260(8)	0.0228(7)	0.0174(10)	0.0205(6)	0	0
O2	0.0079(6)	0.0105(6)	0.0216(9)	0.0022(5)	0	0
O3a	0.024(2)	0.0139(7)	0.0093(9)	0.0111(8)	−0.0063(10)	−0.0032(5)
O4a, O4b*	0.0116(10)	= U_{11}	0.071(12)	= U_{11}/2	0	0

* U_{ij}(O4a) = U_{ij}(O4b), R_1:0.0611, wR_2 : 0.0959, $\Delta\rho_{max}$ / $\Delta\rho_{min}$: 0.56 /−0.33 fm Å^{-3}

(B) Crystal structure analysis of single-crystal X-ray diffraction data of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$

The single-crystal X-ray diffraction analysis was also carried out for $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$. The refinement of the occupancy factors gave g(La2) = 0.891(3), g(Si) = 0.981(8), g(O3) = 0.79(8) (g(O3b) = 1 – g(O3) = 0.21) and g(O4) = 0.68(3) (g(O4b) = (1 – g(O4)) / 2 = 0.158) which agree well with the result of the neutron diffraction analysis. The final structure refinements based on the single-crystal X-ray diffraction data were carried out fixing the occupancy factors of cations to theoretical values (i.e. g(La1) = 0.8912, g(La2) = 1 and g(Si) = 0.971). Thus, the X-ray diffraction analysis also supported the Si-vacancy model for this material. The atomic coordinates agree within 3σ between the neutron and X-ray results.

Table S7. Atomic Coordinates and Atomic Displacement Parameters Refined using Single-Crystal X-Ray Diffraction Data of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$, Based on the Si-Vacancy Model with O3 and O4 Non-Split Sites and without Interstitial Oxygens.

Site	Wyckoff position	g	x	y	z	U_{eq} (Å^2)
La1	4*f*	0.8912	1/3	2/3	–0.00089(8)	0.01465(12)
La2	6*h*	1	0.01211(4)	0.23911(4)	1/4	0.01211(9)
Si	6*h*	0.971	0.40287(18)	0.37267(19)	1/4	0.0084(3)
O1	6*h*	1	0.3261(6)	0.4864(6)	1/4	0.0189(9)
O2	6*h*	1	0.5960(5)	0.4729(5)	1/4	0.0163(9)
O3	12*i*	1	0.3476(5)	0.2565(4)	0.0694(5)	0.0270(8)
O4	2*a*	1	0	0	1/4	0.097(7)

Site	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)	U_{13} (Å^2)	U_{23} (Å^2)
La1	0.01132(14)	= U_{11}	0.0213(3)	= U_{11}/2	0	0
La2	0.00983(15)	0.01317(16)	0.01207(17)	0.00481(13)	0	0
Si	0.0097(7)	0.0086(7)	0.0076(8)	0.0051(6)	0	0
O1	0.026(2)	0.026(2)	0.014(2)	0.021(2)	0	0
O2	0.0105(19)	0.015(2)	0.020(2)	0.0042(17)	0	0
O3	0.051(2)	0.0188(16)	0.0142(17)	0.0200(16)	–0.0131(16)	–0.0049(14)
O4	0.016(3)	= U_{11}	0.26(2)	= U_{11}/2	0	0

R_1 : 0.0207, wR_2 : 0.0412, $\Delta\rho_{max}$ / $\Delta\rho_{min}$: 1.56 / –1.26 e Å^{-3}

Table S8. Atomic Coordinates and Atomic Displacement Parameters Refined using Single-Crystal X-Ray Diffraction Data of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$, Based on the Si-Vacancy Model with O3a and O3b Split Sites, with O4 Non-Split Site and without Interstitial Oxygens.

Site	Wyckoff position	*g*	*x*	*y*	*z*	U_{eq} (Å^2)
La1	4*f*	0.8912	1/3	2/3	–0.00089(8)	0.01462(11)
La2	6*h*	1	0.01211(4)	0.23910(4)	1/4	0.01210(9)
Si	6*h*	0.971	0.40285(18)	0.37265(18)	1/4	0.0084(3)
O1	6*h*	1	0.3260(6)	0.4863(6)	1/4	0.0190(9)
O2	6*h*	1	0.5960(5)	0.4728(5)	1/4	0.0163(9)
O3a	12*i*	0.84(2)	0.3543(6)	0.2582(5)	0.0665(6)	0.0180(9)
O4	2*a*	1	0	0	1/4	0.096(7)
O3b	12*i*	0.16 =(1−*g*(O3a))	0.303(2)	0.246(3)	0.090(3)	U_{iso} 0.004(5)

Site	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)	U_{13} (Å^2)	U_{23} (Å^2)
La1	0.01128(13)	= U_{11}	0.0213(3)	= U_{11}/2	0	0
La2	0.00982(15)	0.01316(16)	0.01205(16)	0.00480(12)	0	0
Si	0.0097(7)	0.0085(7)	0.0076(7)	0.0051(6)	0	0
O1	0.026(2)	0.026(2)	0.014(2)	0.020(2)	0	0
O2	0.0103(19)	0.015(2)	0.020(2)	0.0039(17)	0	0
O3a	0.028(3)	0.019(2)	0.011(2)	0.015(2)	–0.0027(16)	–0.004(2)
O4	0.016(3)	= U_{11}	0.26(2)	= U_{11}/2	0	0

R_1 : 0.0201, wR_2 : 0.0400, $\Delta\rho_{max}$ / $\Delta\rho_{min}$: 1.55 / –1.26 *e* Å^{-3}

Table S9. Atomic Coordinates and Atomic Displacement Parameters Refined using Single-Crystal X-Ray Diffraction Data of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$, Based on the Si-Vacancy Model with O3 Non-Split Site, with O4a and O4b Split Sites and without Interstitial Oxygens.

Site	Wyckoff position	*g*	*x*	*y*	*z*	U_{eq} (Å^2)
La1	4*f*	0.8912	1/3	2/3	–0.00089(8)	0.01463(11)
La2	6*h*	1	0.01211(4)	0.23911(4)	1/4	0.01211(9)
Si	6*h*	0.971	0.40287(19)	0.37267(18)	1/4	0.0084(3)
O1	6*h*	1	0.3261(6)	0.4863(6)	1/4	0.0190(9)
O2	6*h*	1	0.5960(5)	0.4729(5)	1/4	0.0164(9)
O3	12*i*	1	0.3476(5)	0.2565(4)	0.0694(5)	0.0270(8)
O4a = O4	2*a*	0.68	0	0	1/4	0.038(5)
O4b	12*i*	0.16 =(1−*g*(O4a))/2	0	0	0.138(9)	= O4

Site	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)	U_{13} (Å^2)	U_{23} (Å^2)
La1	0.01132(14)	= U_{11}	0.0212(3)	= U_{11}/2	0	0
La2	0.00983(15)	0.01317(16)	0.01209(17)	0.00481(13)	0	0
Si	0.0097(7)	0.0086(7)	0.0076(8)	0.0051(6)	0	0
O1	0.026(2)	0.026(2)	0.015(2)	0.021(2)	0	0
O2	0.0105(19)	0.015(2)	0.020(2)	0.0042(17)	0	0
O3	0.051(2)	0.0187(16)	0.0142(17)	0.0200(16)	–0.0130(16)	–0.0048(14)
O4a, O4b*	0.015(3)	= U_{11}	0.084(17)	= U_{11}/2	0	0

* U_{ij}(O4a) = U_{ij}(O4b), R_1 : 0.0205, wR_2 : 0.0406, $\Delta\rho_{max}$ / $\Delta\rho_{min}$: 1.56 / –1.26 *e* Å^{-3}

Table S10. Atomic Coordinates and Atomic Displacement Parameters Refined using Single-Crystal X-Ray Diffraction Data of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$, Based on the Si-Vacancy Model with O3a, O3b, O4a and O4b Split Sites and without Interstitial Oxygens (**Final Refinement of X-Ray Data of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$**).

Site	Wyckoff position	*g*	*x*	*y*	*z*	U_{eq} (Å^2)
La1	4*f*	0.8912	1/3	2/3	−0.00089(8)	0.01460(11)
La2	6*h*	1	0.01211(4)	0.23910(4)	1/4	0.01210(9)
Si	6*h*	0.971	0.40286(18)	0.37264(18)	1/4	0.0084(3)
O1	6*h*	1	0.3260(6)	0.4863(6)	1/4	0.0190(9)
O2	6*h*	1	0.5960(5)	0.4728(5)	1/4	0.0164(9)
O3a	12*i*	1	0.3543(6)	0.2582(5)	0.0665(6)	0.0181(9)
O4a = O4	2*a*	0.68	0	0	1/4	0.038(5)
O3b	12*i*	0.16	0.303(2)	0.246(3)	0.090(3)	U_{iso} 0.004(5)
O4b	4*e*	0.159	0	0	0.138(8)	0.038(5)

Site	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)	U_{13} (Å^2)	U_{23} (Å^2)
La1	0.01129(13)	= U_{11}	0.0212(3)	= U_{11}/2	0	0
La2	0.00981(15)	0.01315(16)	0.01207(16)	0.00480(12)	0	0
Si	0.0097(7)	0.0085(7)	0.0075(7)	0.0051(6)	0	0
O1	0.026(2)	0.026(2)	0.015(2)	0.020(2)	0	0
O2	0.0103(19)	0.015(2)	0.020(2)	0.0040(16)	0	0
O3a	0.028(3)	0.019(2)	0.011(2)	0.015(2)	−0.003(2)	−0.0026(15)
O4a, O4b*	0.015(3)	= U_{11}	0.084(16)	= U_{11}/2	0	0

* U_{ij}(O4a) = U_{ij}(O4b), R_1: 0.0199, wR_2: 0.0391, $\Delta\rho_{max}$ / $\Delta\rho_{min}$: 1.55 / –1.27 *e* Å^{-3}

(C) Density functional theory (DFT) based calculations

Density functional theory (DFT)-based structural optimization of $La_{76}(Si_{47}\square)O_{208}$ with an Si vacancy $\square$ and without interstitial oxygens was successfully performed (Fig. 3). Table S11 shows that the averaged atomic coordinates of optimized $La_{76}(Si_{47}\square)O_{208}$ agree well with those refined with single-crystal neutron data of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$. DFT-based structural optimization was also applied to $La_{58}Si_{36}O_{159}$ with three interstitial oxygen atoms (2 × 1 × 3 supercell, the interstitial model with the corresponding chemical formula of $La_{9.667}Si_6O_{26.5}$). The calculation condition of this $La_{58}Si_{36}O_{159}$ was the same as that of $La_{76}(Si_{47}\square)O_{208}$ (Si-vacancy model) except the *k*-point mesh of 3×3×1. This interstitial model is the same as that reported by Jones et al.[17] and the initial atomic coordinates of the interstitial oxygen atoms were imported from this literature. The formation energies (heats of formation, formation enthalpies) of $La_{58}Si_{36}O_{159}$ and $La_{76}(Si_{47}\square)O_{208}$ were evaluated using the following equations.

$29\ La_2O_3 + 36\ SiO_2 \rightarrow La_{58}Si_{36}O_{159}$ (interstitial model) (S1)

$38\ La_2O_3 + 47\ SiO_2 \rightarrow La_{76}(Si_{47}\square)O_{208}$ (Si-vacancy model without interstitial oxygens) (S2)

The formation energy of $La_{58}Si_{36}O_{159}$ with three interstitial oxygens in equation (S1) was calculated to be −32.046 eV. The calculated formation energy of $La_{76}(Si_{47}\square)O_{208}$ with an Si vacancy in equation (S2) was −48.122 eV. Therefore, it is suggested that both reactions (S1) and (S2) are energetically favorable.

$La_{58}Si_{36}O_{159}$ (interstitial model) + $5.125\ La_2SiO_5$

$\rightarrow\ 0.875\ La_{76}(Si_{47}\square)O_{208}$ (Si-vacancy model without interstitial oxygens) (S3)

The formation energy of 0.875 $La_{76}(Si_{47}\square)O_{208}$ in equation (S3) was estimated to be + 11.115 eV, which is equaled to +43.9 meV per atom, which is too small to determine the energetically favorable model. Therefore, the present DFT calculations show that the Si-deficient is possible to form.

Table S11. Comparison of the Fractional Coordinates (x_{DFT}, y_{DFT}, z_{DFT}) Obtained by the DFT-Based Structural Optimization of $La_{76}(Si_{47}\square)O_{208}$ (Si-vacancy model), with Those (x_{ND}, y_{ND}, z_{ND}) Refined Using the Single-Crystal Neutron-Diffraction (ND) Data of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$.

	DFT			**Single-crystal neutron diffraction**			**Difference**		
Site	x_{DFT}	y_{DFT}	z_{DFT}	x_{ND}	y_{ND}	z_{ND}	$x_{DFT} - x_{ND}$	$y_{DFT} - y_{ND}$	$z_{DFT} - z_{ND}$
La1	0.334(7)	0.668(8)	−0.010(12)	1/3	2/3	−0.0010(2)	0.00035	0.00124	−0.00931
La2	0.010(8)	0.243(5)	0.251(5)	0.01213(10)	0.23936(10)	1/4	−0.00219	0.00352	0.00121
Si	0.401(4)	0.370(5)	0.249(4)	0.40316(19)	0.37291(19)	1/4	−0.00258	−0.00274	−0.00058
O1	0.322(14)	0.484(14)	0.247(11)	0.32493(18)	0.48610(18)	1/4	−0.00323	−0.00177	−0.00254
O2	0.595(6)	0.471(6)	0.248(10)	0.59574(15)	0.47295(15)	1/4	−0.00076	−0.00180	−0.00190
O3	0.342(16)	0.252(7)	0.068(9)	0.3528(7)	0.2581(2)	0.0665(4)	−0.01100	−0.00610	0.00184
O4	0.001(3)	−0.001(3)	0.249(6)	0	0	1/4	0.00109	−0.00078	−0.00093

The fractional coordinates (x_{DFT}, y_{DFT}, z_{DFT}) were calculated by converting the fractional coordinates of the 2 × 2 × 2 supercell $La_{76}(Si_{47}\square)O_{208}$) into the corresponding ones in the 1 × 1× 1 unit cell of $La_{9.5}(Si_{5.875}\square_{0.125})O_{26}$. The fractional coordinates (x_{DFT}, y_{DFT}, z_{DFT}) were averaged and the standard deviations were also calculated as shown in parentheses.

(D) Treatment of O3 and O4 in the structure analysis of the time-of-flight neutron data of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$

Difference Fourier maps clearly show the residual density around O3 and O4 sites (Figs. 4a and 4c). The highest residual density (1.13 fm $Å^{-3}$) appeared at (0, 0, 0.144) (observed in Fig. 2c, z = 0.15) which is quite near from the O4 position of (0, 0, 1/4) and the distance between these two positions is 0.76 Å which is too close to be considered as an interstitial site. Also, the negative density was observed at O4 site (clearly observed in Fig. 2c, z = 1/4). Therefore we concluded that O4 is highly disordered along the c axis and we O4 into O4a and O4b as a split site model. The total occupancy factors of O4a and O4b was constrained to be unity and common anisotropic displacement parameters were used for O4a and O4b because it gave better result than using independent isotropic or anisotropic displacement parameter. The second highest residual density (0.78 fm $Å^{-3}$) appeared at (0.284, 0.241, 0.099) (clearly observed in Fig. 2c, z = 0.10) which was 0.61 Å from O3 site (0.3489(2), 0.2565(2), 0.0680(3)). This site is also too close to be considered as an interstitial site. Therefore, O3 was also split into O3a and O3b as a split site model. The total occupancy factor of O3a and O3b was fixed to unity and an anisotropic and isotropic displacement parameters were used for O3a and O3b, respectively.

(E) Results of the single-crystal neutron diffraction analyses of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$ by various interstitial models.

Table S12. Results of the Single-Crystal Neutron Diffraction Analyses of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$ by Various Interstitial Models.

Reference No.		15 (J. Tolchard et al. 2003)			17 (L. León-Reina et al. 2004)	19 (L. León-Reina et al. 2005)	20 (A. Jones et al. 2008)	27 (R. Ali et al. 2008)	24 (K. Matsunaga et al. 2012)	23 (K. Fukuda et al. 2012)	43 (T. An et al. 2014)		
Formula in the literature		$La_{9.33}Si_6O_{26}$			$La_{9.55}Si_6O_{26.32}$	$La_{9.33}Si_{0.5}Ge_{0.5}O_{26}$	$La_{9.67}Si_6O_{26.5}$	$La_{9.69}Si_{5.70}Mg_{0.30}O_{26.24}$	$La_{9.33}Si_6O_{26}$	$La_{9.50}Si_6O_{26.25}$	$Nd_8Sr_2Si_6O_{26}$		
Methods used in the literature*		DFT			Joint PXRD PND	Joint PXRD PND	DFT	PND	DFT	SXRD	SND		
Label used in the literature		O6	O7	O7'	O5	O5	O5	O5	O5	O5	$O_{int}1$	$O_{int}2$	$O_{int}3$
Wyckoff position		2*b*	12*i*	12*i*	12*i*	12*i*	12*i*	12*i*	12*i*	6*h*	6*h*	6*h*	12*i*
x		0	0.0135	0.013	–0.001	0.005	0.0045	–0.004	0	0.27	0.7375	0.3684	0.1533
y		0	0.2333	0.2326	0.224	0.242	0.2223	0.24	0.09	0.08	0.2011	0.101	0.4994
z		1/2	0.8763	0.6246	0.58	0.61	0.6309	0.6	0.35	1/4	1/4	1/4	0.1574
Analysis-1	R_1	0.1004	0.0708	0.0708	0.0703	0.0707	0.0707	0.0706	0.0704	0.0778	0.0770	0.0790	0.0699
	wR_2	0.1230	0.1013	0.1013	0.1012	0.1016	0.1016	0.1016	0.1013	0.1060	0.1057	0.1063	0.1012
	$g(O_{int})$	0.387500	0.064583	0.064583	0.064583	0.064583	0.064583	0.064583	0.064583	0.129167	0.129167	0.129167	0.064583
Analysis-2	R_1	0.0621	0.0622	0.0622	0.0622	0.0622	0.0622	0.0622	0.0622	0.0622	0.0622	0.0622	0.0622
	wR_2	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965
	$g(O_{int})$	–0.015(9)	0.002(3)	0.002(3)	0.002(3)	0.000(3)	0.000(3)	–0.001(3)	0.000(3)	0.000(5)	0.001(5)	–0.003(5)	0.002(3)
Analysis-3	R_1		0.0697	0.0697	0.0696	0.0697	0.0697	0.0696	0.0694	0.0772	0.0780	0.0778	0.0700
	wR_2		0.1005	0.1005	0.1005	0.1005	0.1005	0.1005	0.1004	0.1053	0.1051	0.1052	0.1007
	x	–	0.033(2)	0.033(2)	0.0262(19)	0.033(2)	0.033(2)	0.0262(19)	0.0305(19)	0.2364(14)	0.7073(14)	0.3445(14)	0.1475(18)
	y		0.2139(19)	0.2139(19)	0.2112(19)	0.2139(19)	0.2139(19)	0.2112(19)	0.1121(18)	0.0611(14)	0.2100(14)	0.0675(14)	0.4790(19)
	z		0.914(3)	0.586(3)	0.576(3)	0.586(3)	0.586(3)	0.576(3)	0.321(3)	1/4	1/4	1/4	0.185(2)
	$g(O_{int})$	0.387500	0.064583	0.064583	0.064583	0.064583	0.064583	0.064583	0.064583	0.129167	0.129167	0.129167	0.064583

The position of the interstitial sites were imported from the previously reported literature. In the *Analysis*-1, the atomic coordinates were fixed to reported values and occupancy factor was fixed to the ideal value. In the *Analysis*-2, the atomic coordinates were fixed to reported values and occupancy factor was refined. In the *Analysis*-3, the atomic coordinates were refined and occupancy factor was fixed to the ideal value. In all refinements, *g*(La1) was fixed to 0.9625 and the other occupancy factors were fixed to unity. * DFT: Density Functional Theory. PND: Powder Neutron Diffraction. PXRD: Powder X-Ray Diffraction. SXRD: Synchrotron X-Ray Diffraction. SND: Single-crystal Neutron Diffraction.

Table S12(continued). Results of the Single-Crystal Neutron Diffraction Analyses of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$ by Various Interstitial Models.

Reference No.		45 (E. Béchade et al. 2009)	22 (T. Liao et al. 2011)						44 (T. An et al. 2016)							
Formula in the literature		$La_{9.33}Si_6O_{26}$	$La_{9.33}Si_6O_{26}$			$Nd_{9.33}Si_6O_{26}$ (4 K)					$Nd_{9.33}Si_6O_{26}$ (100 K)				$Nd_{9.33}Si_6O_{26}$ (300 K)	
Methods used in the literature		DFT	DFT								SND					
Label used in the literature		O5	O_i	O_i'	$O_{Int}1$	$O_{Int}2$	$O_{Int}3$	$O_{Int}4$	$O_{Int}1$	$O_{Int}2$	$O_{Int}3$	$O_{Int}4$	$O_{Int}5$	$O_{Int}1$	$O_{Int}2$	$O_{Int}3$
Wyckoff position		12*i*	12*i*	12*i*	12*i*	12*i*	12*i*	12*i*	6*h*	12*i*	12*i*	12*i*	12*i*	12*i*	12*i*	12*i*
x		0.106	-0.0820	0.0117	0.1429	0.0832	0.0003	0.7622	0.7302	0.1431	0.0002	0.0686	0.3865	0.1300	0.0001	0.5079
y		0.0177	-0.0964	0.1051	0.3981	0.3085	0.0003	0.0851	0.1313	0.4042	0.0002	0.4393	0.1276	0.4034	0.0001	0.1627
z		0.588	0.6093	0.9144	0.0361	0.0554	0.1539	0.2163	1/4	0.0382	0.1434	0.0279	0.024	0.037	0.1304	0.0358
Analysis-1	R_1	0.691	0.678	0.678	0.0709	0.0696	0.0824	0.0725	0.0778	0.0707	0.0824	0.0699	0.0704	0.070	0.071	0.0712
	wR_2	0.1009	0.1002	0.1002	0.1015	0.1005	0.1099	0.102	0.1051	0.1014	0.11	0.1012	0.1015	0.1016	0.1023	0.1029
	$g(O_{int})$	0.064583	0.032292	0.032292	0.064583	0.064583	0.064583	0.064583	0.129167	0.064583	0.064583	0.064583	0.064583	0.064583	0.064583	0.064583
Analysis-2	R_1	0.622	0.622	0.622	0.0622	0.0622	0.0621	0.0622	0.0622	0.0622	0.0621	0.0622	0.0622	0.0622	0.0623	0.0622
	wR_2	0.965	0.965	0.965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0963
	$g(O_{int})$	0.001(3)	-0.002(4)	0.003(4)	0.000(3)	0.004(3)	-0.001(2)	0.002(3)	0.007(5)	0.000(3)	-0.001(2)	-0.002(3)	0.000(3)	0.000(3)	-0.005(3)	-0.014(3)
Analysis-3	R_1	0.0627	0.0622	0.0622	0.0679	0.0681	diverged	0.0687	0.0767	0.0679	diverged	0.0679	0.069	0.0687	0.0693	0.0695
	wR_2	0.0966	0.0961	0.0961	0.0999	0.0999		0.0999	0.1048	0.0999		0.0999	0.0999	0.1004	0.1002	0.1011
	x	0.0485(19)	-0.067(3)	0.002(5)	0.0948(19)	0.0851(18)		0.7595(19)	0.7340(13)	0.0948(19)		0.0948(19)	0.3852(18)	0.1706(18)	0.024(2)	0.489(3)
	y	-0.007(2)	-0.097(3)	0.057(4)	0.4193(18)	0.3263(19)		0.1124(19)	0.1113(14)	0.4193(18)		0.4193(18)	0.1756(19)	0.3634(19)	0.0152(19)	0.188(2)
	z	0.535(2)	0.696(4)	0.968(5)	0.000(3)	0.009(3)		0.187(2)	1/4	0.000(3)		0.000(3)	-0.007(3)	0.0515(19)	0.1726(18)	0.052(3)
	$g(O_{int})$	0.064583	0.032292	0.032292	0.064583	0.064583		0.064583	0.129167	0.064583		0.064583	0.064583	0.064583	0.064583	0.064583

Table S12(continued). Results of the Single-Crystal Neutron Diffraction Analyses of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$ by Various Interstitial Models.

Reference No.		44 (T. An et al. 2016)													
Formula in the literature		$Nd_{9.33}Si_6O_{26}$ (573 K)					$Nd_{9.33}Si_6O_{26}$ (773 K)								
Methods used in the literature		SND													
Label used in the literature		$O_{Int}1$	$O_{Int}2$	$O_{Int}3$	$O_{Int}4$	$O_{Int}5$	$O_{Int}1$	$O_{Int}2$	$O_{Int}3$	$O_{Int}4$	$O_{Int}5$	$O_{Int}6$	$O_{Int}7$	$O_{Int}8$	$O_{Int}9$
Wyckoff position		12*i*	12*i*	12*i*	12*i*	12*i*	6*h*	6*h*	6*h*	12*i*	6*h*	6*h*	12*i*	6*h*	12*i*
x		0.1507	0.6248	0.9891	0.0643	0.5911	0.5056	0.2381	0.3575	0.8912	0.4492	0.0513	0.1348	0.1388	0.9406
y		0.3933	0.0643	0.895	0.9214	0.8222	0.0271	0.406	0.4281	0.0109	0.0246	0.4567	0.4017	0.3053	0.0052
z		0.0354	0.0557	0.0596	0.0932	0.0674	1/4	1/4	1/4	0.036	1/4	1/4	0.0454	1/4	0.0875
Analysis-1	R_1	0.0711	0.0699	0.0686	0.0706	0.0706	0.0774	0.0781	0.0708	0.0702	0.079	0.0795	0.0703	0.0795	0.0665
	wR_2	0.1016	0.1008	0.1004	0.1018	0.1013	0.1056	0.1064	0.1013	0.1014	0.1053	0.1072	0.1013	0.1067	0.0992
	$g(O_{int})$	0.0645833	0.0645833	0.0645833	0.0645833	0.0645833	0.129167	0.129167	0.129167	0.0645833	0.129167	0.129167	0.0645833	0.129167	0.0645833
Analysis-2	R_1	0.0622	0.0622	0.062	0.0622	0.0622	0.0621	0.0622	0.0622	0.0622	0.0622	0.0621	0.0622	0.0622	0.0614
	wR_2	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0964	0.0965	0.0965	0.0962
	$g(O_{int})$	0.000(3)	0.005(3)	0.006(4)	-0.004(3)	0.000(3)	0.004(5)	0.000(5)	0.001(5)	-0.001(3)	0.002(5)	-0.010(4)	0.002(3)	-0.004(4)	0.015(3)
Analysis-3	R_1	0.0684	0.0695	0.0627	0.0701	0.0689	0.0764	0.0768	0.0777	0.0627	0.0764	0.078	0.0679	0.0753	0.0627
	wR_2	0.0999	0.0997	0.0966	0.1005	0.0999	0.1037	0.1045	0.1057	0.0966	0.1037	0.105	0.0999	0.1035	0.0966
	x	0.1574(19)	0.5906(19)	0.993(2)	0.0900(19)	0.6202(19)	0.4771(13)	0.2753(13)	0.3338(13)	0.9515(19)	0.4771(13)	0.1327(14)	0.0948(19)	0.1610(14)	0.9515(19)
	y	0.3517(19)	0.0390(18)	0.9442(17)	0.9346(19)	0.8287(19)	0.0434(13)	0.3951(14)	0.4154(14)	0.007(2)	0.0434(13)	0.4730(14)	0.4193(18)	0.2478(13)	0.007(2)
	z	0.001(3)	0.099(3)	0.035(2)	0.181(3)	0.008(3)	1/4	1/4	1/4	0.035(2)	1/4	1/4	0.000(3)	1/4	0.035(2)
	$g(O_{int})$	0.0645833	0.0645833	0.0645833	0.0645833	0.0645833	0.129167	0.129167	0.129167	0.0645833	0.129167	0.129167	0.0645833	0.129167	0.0645833

Table S12(continued). Results of the Single-Crystal Neutron Diffraction Analyses of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$ by Various Interstitial Models.

Reference No.		44 (T. An et al. 2016)														
Formula in the literature		$Nd_{28.5/3}Al_{0.5}Si_{5.5}O_{26}$ 100K						$Nd_{29/3}AlSi_5O_{26}$ 100K					$Nd_{29.5/3}Al_{1.5}Si_{4.5}O_{26}$ 100K			
Methods used in the literature		SND														
Label used in the literature		$O_{Int}1$	$O_{Int}2$	$O_{Int}3$	$O_{Int}4$	$O_{Int}5$	$O_{Int}6$	$O_{Int}7$	$O_{Int}1$	$O_{Int}2$	$O_{Int}3$	$O_{Int}4$	$O_{Int}5$	$O_{Int}1$	$O_{Int}2$	$O_{Int}3$	$O_{Int}4$
Wyckoff position		12*i*	12*i*	12*i*	6*h*	6*h*	6*h*	12*i*	12*i*	12*i*	12*i*	12*i*	12*i*	6*h*	6*h*	6*h*	6*h*
x		0.6888	0.8069	0.9272	0.7760	0.8026	0.4142	0.7600	0.0700	0.3816	0.8045	0.5319	0.5545	0.4882	0.6129	0.4471	0.5866
y		0.0324	0.035	−0.0014	0.1509	0.1129	0.5105	0.1197	0.2853	0.5552	0.0307	0.1348	0.1557	0.0371	0.1592	0.4636	0.2295
z		0.1431	0.1261	0.1058	1/4	1/4	1/4	0.1625	0.1405	0.1616	0.1096	0.0377	0.1357	1/4	1/4	1/4	1/4
Analysis-1	R_1	0.071	0.0706	0.069	0.0709	0.0793	0.0762	0.0689	0.0716	0.0706	0.0705	0.0703	0.0698	0.0765	0.0792	0.079	0.0785
	wR_2	0.1013	0.1009	0.1007	0.1015	0.1059	0.1046	0.1005	0.1019	0.1014	0.1008	0.102	0.1008	0.1043	0.1067	0.1065	0.106
	$g(O_{int})$	0.064583	0.064583	0.064583	0.129167	0.129167	0.129167	0.064583	0.064583	0.064583	0.064583	0.064583	0.064583	0.129167	0.129167	0.129167	0.129167
Analysis-2	R_1	0.0622	0.0622	0.0618	0.0622	0.0622	0.0622	0.0622	0.0621	0.0622	0.0622	0.0622	0.0621	0.0621	0.0621	0.0621	0.0622
	wR_2	0.0965	0.0965	0.0964	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0964	0.0965	0.0964	0.0965	0.0965	0.0965
	$g(O_{int})$	0.001(3)	0.004(3)	0.007(3)	0.003(5)	-0.001(2)	0.007(5)	0.002(3)	-0.005(4)	-0.003(3)	0.004(3)	-0.007(3)	0.004(3)	0.012(5)	-0.004(2)	-0.003(3)	-0.001(2)
Analysis-3	R_1	0.0695	0.0697	0.0627	0.0762	0.0763	0.076	0.0687	0.0697	0.0686	0.0697	0.0682	0.0688	0.0764	0.0745	0.0764	0.0786
	wR_2	0.1004	0.1005	0.0966	0.1044	0.1044	0.1045	0.0999	0.1007	0.1008	0.1005	0.0996	0.0999	0.1037	0.1032	0.1046	0.1058
	x	0.6351(19)	0.8193(19)	0.9515(19)	0.7711(13)	0.7709(13)	0.4134(13)	0.7595(19)	0.0661(19)	0.4108(19)	0.8193(19)	0.5415(19)	0.5273(18)	0.4771(13)	0.5181(13)	0.4187(13)	0.5733(13)
	y	-0.0304(19)	0.033(2)	0.007(2)	0.1257(13)	0.1231(13)	0.5170(13)	0.1124(19)	0.3087(19)	0.5865(18)	0.033(2)	0.1832(18)	0.1214(19)	0.0434(13)	0.1086(14)	0.5121(13)	0.2322(13)
	z	0.124(3)	0.086(3)	0.035(2)	0.25	0.25	0.25	0.187(2)	0.188(2)	0.186(2)	0.086(3)	0.003(3)	0.139(3)	0.25	0.25	0.25	0.25
	$g(O_{int})$	0.064583	0.064583	0.064583	0.129167	0.129167	0.129167	0.064583	0.064583	0.064583	0.064583	0.064583	0.064583	0.129167	0.129167	0.129167	0.129167

Table S12(continued). Results of the Single-Crystal Neutron Diffraction Analyses of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$ by Various Interstitial Models.

Reference No.		44 (T. An et al. 2016)												
Formula in the literature		$Nd_{9.33}Si_6O_{26}$ As Grown						$Nd_{9.33}Si_6O_{26}$ Annealed						
Methods used in the literature		SND												
Label used in the literature		$O_{Int}1$	$O_{Int}2$	$O_{Int}3$	$O_{Int}4$	$O_{Int}5$	$O_{Int}6$	$O_{Int}1$	$O_{Int}2$	$O_{Int}3$	$O_{Int}4$	$O_{Int}5$	$O_{Int}6$	$O_{Int}7$
Wyckoff position		12*i*	12*i*	12*i*	6*h*	12*i*	12*i*	6*h*	6*h*	12*i*	12*i*	12*i*	12*i*	6*h*
x		0.9844	0.1003	0.7409	0.6952	0.5358	0.3958	0.7527	0.8184	0.0819	0.3858	0.5423	0.4169	0.1688
y		0.0042	0.3392	0.0887	0.8210	0.1373	0.5243	0.0505	0.1413	0.3374	0.5979	0.1386	0.5739	0.1724
z		0.0618	0.0574	0.1930	1/4	0.1276	0.1206	1/4	1/4	0.0478	0.1666	0.0868	0.0634	1/4
Analysis-1	R_1	0.0764	0.0698	0.0697	0.0787	0.0694	0.0702	0.0768	0.0784	0.0696	0.0698	0.0697	0.0714	0.0797
	wR_2	0.1052	0.1003	0.1003	0.1066	0.1001	0.1005	0.1051	0.1057	0.1002	0.1015	0.1009	0.1017	0.1071
	$g(O_{int})$	0.0645833	0.0645833	0.0645833	0.129167	0.0645833	0.0645833	0.129167	0.129167	0.0645833	0.0645833	0.0645833	0.0645833	0.129167
Analysis-2	R_1	0.0622	0.0623	0.0621	0.0622	0.0621	0.0623	0.0622	0.0622	0.0623	0.0623	0.0622	0.0621	0.0622
	wR_2	0.0965	0.0965	0.0965	0.0965	0.0964	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965	0.0965
	$g(O_{int})$	0.000(3)	0.005(3)	0.006(3)	-0.001(2)	0.008(3)	0.006(3)	0.004(5)	-0.001(2)	0.007(3)	-0.004(3)	0.001(3)	-0.003(4)	-0.003(2)
Analysis-3	R_1	0.0627	0.0681	0.0687	0.0753	0.0689	0.0689	0.0766	0.0762	0.0681	0.0689	0.0689	0.0689	0.0755
	wR_2	0.0966	0.0999	0.0999	0.1035	0.0999	0.0999	0.1047	0.1044	0.0999	0.1003	0.0999	0.0999	0.1035
	x	0.9515(19)	0.0851(18)	0.7595(19)	0.7522(13)	0.5276(18)	0.4138(18)	0.7367(14)	0.7711(13)	0.0851(18)	0.3741(18)	0.5276(18)	0.4138(18)	0.1657(14)
	y	0.007(2)	0.3263(19)	0.1124(19)	0.9132(14)	0.1229(19)	0.5229(18)	0.0410(13)	0.1257(13)	0.3263(19)	0.6124(18)	0.1229(19)	0.5229(18)	0.2497(13)
	z	0.035(2)	0.009(3)	0.187(2)	1/4	0.137(3)	0.105(3)	1/4	1/4	0.009(3)	0.197(2)	0.137(3)	0.105(3)	1/4
	$g(O_{int})$	0.0645833	0.0645833	0.0645833	0.129167	0.0645833	0.0645833	0.129167	0.129167	0.0645833	0.0645833	0.0645833	0.0645833	0.129167

(F) Difference Fourier maps of the Single-Crystal X-Ray Diffraction Data of $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$

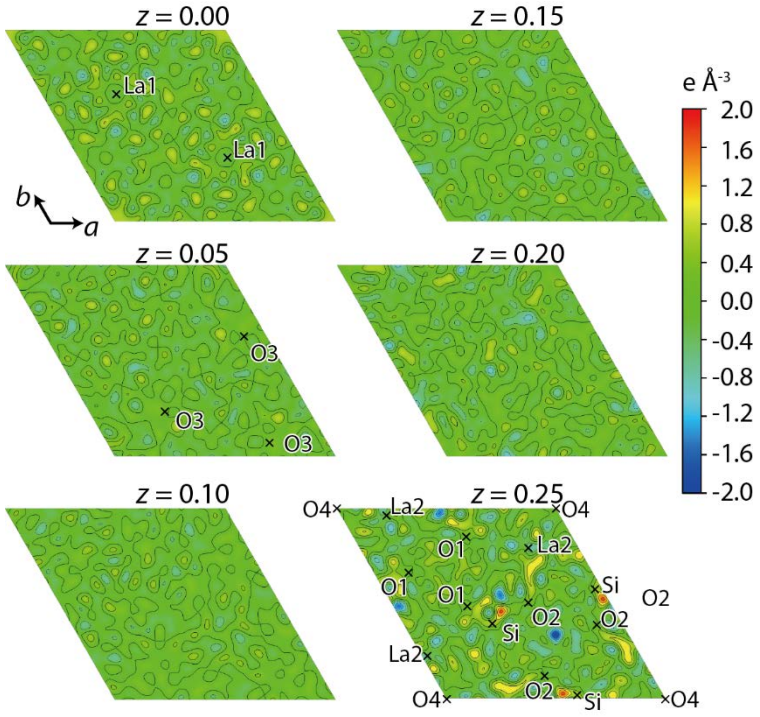

Figure S1. Difference Fourier maps on the *ab* planes at six different *z* values obtained by the single-crystal X-ray diffraction analysis of the basic material $La_{9.565}(Si_{5.826}\square_{0.174})O_{26}$. $\Delta\rho_{max}$ / $\Delta\rho_{min}$ = 1.55 / −1.27 *e* Å^{-3}. No significant peaks indicating no interstitial oxygens. Contours from –1.0 to 1.0 *e* Å^{-3} by 0.2 *e* Å^{-3} step.

End of the Supplementary Information.