

Ionic-Layer Engineering Enables Propeller-Type Interstitialcy Oxygen Migration in Close-Packed Perovskite Solid Electrolytes

Xiaojun Kuang

kuangxiao.jun@gnnu.edu.cn

Gannan Normal University <https://orcid.org/0000-0003-2975-9355>

Yang Zhou

Guilin University of Technology

Xiaohui Li

Guilin University of Technology <https://orcid.org/0009-0007-3620-619X>

Cheng Li

Oak Ridge National Laboratory <https://orcid.org/0000-0002-6546-6413>

Zhenhong Tan

Kyoto University <https://orcid.org/0009-0003-9416-7644>

Ping Miao

Institute of High Energy Physics, Chinese Academy of Sciences <https://orcid.org/0000-0003-1937-1736>

Qi-long Gao

Zhengzhou University

Kun Lin

University of Science and Technology Beijing <https://orcid.org/0000-0003-4515-3206>

Junliang Sun

Peking University <https://orcid.org/0000-0003-4074-0962>

Xianran Xing

University of Science and Technology Beijing <https://orcid.org/0000-0003-0704-8886>

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Abstract

Oxide-ion solid electrolytes (SEs) are key enablers of high-temperature electrochemical energy conversion, catalysis, membrane separation, and electrolyser technologies. However, developing oxide-ion SEs with distinct transport architectures remains challenging, particularly for engineering interstitial oxide-ion conduction in close-packed perovskite structures. Here we address this challenge through an ionic-layer engineering principle rooted in classical perovskite foundations. Inspired by the rock-salt layers in Ruddlesden-Popper phases, highly coordinated alkaline-earth sublattices in close-packed perovskite-derived frameworks are reinterpreted as flexible ionic-layer motifs for interstitial oxygen accommodation and migration. In the complex perovskite $\text{Ca}_{4-x}\text{La}_x\text{Nb}_2\text{O}_{9+x/2}$, reformulated as $\text{Ca}_{3-x}\text{La}_x\text{Ca}'\text{Nb}''_2\text{O}_{9+x/2}$, La substitution restructures the $[\text{Ca}'\text{O}_6]$ ionic layer and promotes interstitial oxygen species incorporation. These interstitials dynamically couple to flexible CaO_{6+x} polyhedra, generating correlated disorder that forms a dynamic network of low-energy migration gateways, enabling propeller-type interstitialcy migration dynamics involving correlated torsional and cage-deformation motions A- and B'-sublattice coordination environments around rigid NbO_6 octahedra, with an activation energy of ~ 0.63 eV. Extension to close-packed double-perovskite framework through modulation of ionic-layer number and connectivity enables control over interstitial-oxygen accommodation and transport, demonstrating that these ionic-layer characteristics can serve as designable structural parameters across distinct perovskite-derived architectures. More broadly, these findings identify transferable ionic-layer motifs as structural descriptors for modulating interstitial oxygen defect chemistry and propeller-type transport in close-packed SEs beyond conventional vacancy-mediated frameworks, and provide a design framework not only for oxide-ion conductors but also for broader perovskite-related functional materials governed by oxygen-defect chemistry and local structural dynamics.

1. Introduction

Oxide-ion solid electrolytes (SEs), which govern ionic transport, have enabled major advances in fuel cells,^{1–3} oxygen separation membranes,⁴ catalytic membrane reactors,^{5,6} high-temperature sensors,⁷ and solid-oxide electrolyzers^{8,9}, thereby fundamentally dictating the performance of these electrochemical technologies. Their functionality arises from the ability of structural frameworks to accommodate and transport oxygen defects over wide temperature windows.^{10,11} Over the past decades, several classical structure families,¹² such as fluorites (e.g., YSZ,¹³ DSC,¹⁴ and $\delta\text{-Bi}_2\text{O}_3$ ¹⁵), pyrochlores,^{16,17} and perovskites¹⁸, LAMOX ($\text{La}_2\text{Mo}_2\text{O}_9$),¹⁹ apatites,²⁰ melilites,²¹ and related open frameworks,^{22–26} have been explored as model systems for correlating defect energetics, migration pathways, and macroscopic transport behavior. However, developing oxide-ion SEs with distinct transport architectures remains challenging, especially when attempting to realize interstitial oxide-ion conduction in close-packed perovskite structures. Here, we revisit long-known close-packed complex perovskites from an ionic-layer perspective, uncover a previously unrecognized interstitial-oxygen

transport motif, and identify an ionic-layer engineering principle in which ionic-layer number, connectivity, and local flexibility can be modulated to regulate interstitial-oxygen accommodation and transport in close-packed perovskites.

Among these classical structure families explored in SEs, perovskites have long served as a cornerstone due to their exceptional chemical and structural versatility.²⁷ In classical close-packed ABO_3 perovskite^{28,29} (Fig. 1a), oxide-ion transport is predominantly governed by oxygen-vacancy-mediated mechanisms, as exemplified by strontium- and magnesium-doped lanthanum gallates $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$,²⁸ and insights gained from leakage-driven transport in perovskite $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$.²⁹ This vacancy-dominated behavior extends broadly to perovskite-derived structures, including double perovskites and hexagonal perovskite-related oxides, where oxide-ion conduction remains closely associated with oxygen deficiency, partial anion occupancy, and structural disorder.^{30–36}

In double perovskites, such as $\text{LnBaM}_2\text{O}_{5+\delta}$ (Ln = lanthanides; M = Co, Fe), the oxygen content is often expressed using an oxygen-hyperstoichiometric notation relative to the oxygen-deficient O_5 parent composition (Fig. 1b). However, when referenced to the fully oxygenated LnBaM_2O_6 framework, they correspond to oxygen-deficient $\text{LnBaM}_2\text{O}_{6-\delta}$ phases. The ordering of A-site cations into alternating Ln-O and Ba-O layers is intrinsically coupled with oxygen deficiency and reduced coordination environments, and oxide-ion conduction remains fundamentally governed by oxygen vacancies rather than interstitial mechanisms.^{30–33} Similarly, in hexagonal perovskite-derived frameworks^{34–36} (Fig. 1c), where face-sharing BO_6 octahedra emerge, their diverse stacking sequences of AO_3 or anion-deficient AO_{3-x} layers with alternating corner-sharing and face-sharing octahedra generate a rich family of structures. Representative systems, such as $9\text{H-Ba}_3\text{MoNbO}_{8.5}$ ³⁴ and $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ based 12R hexagonal perovskites,^{35,36} demonstrate oxide-ion conduction that is intrinsically tied to oxygen deficiency and anion disorder.

Therefore, within classical close-packed perovskite and many perovskite-derived frameworks, oxide-ion transport has historically been dominated by oxygen-vacancy-mediated mechanisms. By contrast, the perovskite-derived layered Ruddlesden-Popper (RP) phases $((\text{AO})(\text{ABO}_3))_n$, Fig. 1d) incorporating rock-salt AO layers into perovskite slabs, could accommodate and transport interstitial oxygen defects within the rock-salt type boundaries of perovskite slabs across $n = 1$ to 3 RP structures,^{37–39} such as $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ (Ln = Lanthanide elements, $n = 1, 2$, and 3).^{40–43} In RP phases, the rock-salt layer acts as a dedicated reservoir and conduction pathway for interstitial species, where mobility is typically governed by a 2D-anisotropic interstitialcy, or push-pull mechanism.^{37,42,44} Beyond RP phases, interstitial transport has also been reported in apatite-, melilite-, and langasite-type materials, which are open-framework or tetrahedrally coordinated structures fundamentally distinct from classical close-packed perovskites.¹²

Although oxide-ion transport in classical close-packed perovskites is predominantly governed by oxygen-vacancy-mediated mechanisms, interstitial oxide-ion conduction has largely been restricted to

structurally open or layered frameworks, highlighting a fundamental structural constraint that has so far limited its realization within close-packed perovskite architectures. A promising and underexplored route is to revisit these classical families to identify previously unrecognized transport motifs hidden within the classical perovskite frameworks, by introducing distinct bonding components into the perovskite network. Herein, inspired by the ionic rock-salt layer in RP structures that can accommodate interstitial oxygen defects, we revisit the defect chemistry in the B-site ordered complex perovskite $A_3B'B''_2O_9$ (B' = alkaline-earth, B'' = transition metal), and identify an ionic-layer engineering principle rooted in classical perovskite frameworks. In this concept, the ionic layer consists of the alkaline-earth-containing B' -site sublattice. The ionic-layer design principle refers to a crystallographically identifiable and structurally flexible sublattice that enables interstitial oxygen accommodation within a classical close-packed framework and activates interstitial oxide-ion migration pathway. We demonstrate that incorporation of highly coordinated alkaline-earth cations at the B' -site as an ionic layer can fundamentally reshape local bonding environments, allowing for the accommodation of excess oxide ions.

In this complex perovskite framework, ordering between the B' and B'' cations gives rise to alternating 1:2 $B'O_6$ and $B''O_6$ octahedral layers. Unlike the relatively rigid $B''O_6$ sublattice, by reinterpreting the alkaline-earth $B'O_6$ octahedral layers similar as rock-salt blocks embedded within the layered RP perovskite matrix (Figs. 1e-f), we uncover their role as unique structurally flexible and adaptable motifs for interstitial oxygen defects. This structural re-description of ordered connectivity provides a new conceptual framework in which oxygen transport is governed by the interplay between rigid and flexible sublattices. Such an ionic-layer engineering principle, rooted in classical perovskite foundations, treats ionic layers as designable structural motifs that leverage the proven stability of classical perovskites while transcending their inherent geometric constraints, opening the door to unconventional defect chemistry and emergent interstitial oxide-ion migration dynamics hidden in long-known classical structures.

Building on this concept of emergent transport motifs in B-site ordered complex perovskites, we focus on the representative case of $Ca_{4-x}La_xNb_2O_{9+x/2}$, which can be reformulated as $Ca_{3-x}La_xCa'Nb''_2O_{9+x/2}$, where B-site ordering of Ca' and Nb'' forms alternating 1:2 $Ca'O_6$ and $Nb''O_6$ octahedral layers (Fig. 1e-f). La substitution at the Ca sublattice restructures the local coordination environment of the Ca' -containing ionic layers and promotes the incorporation of interstitial oxygen defects, thereby activating long-range oxide-ion transport. Furthermore, we combined both average and local structural analysis, including neutron and synchrotron powder diffraction (NPD and SPD), extended X-ray absorption fine structure (EXAFS), and variable-temperature pair distribution function (PDF) analysis with reverse Monte Carlo (RMC) modeling and ab initio molecular dynamics (AIMD) simulations, and reveal that ionic $Ca'O_6$ octahedral layers, analogous to the rock-salt layers in the layered perovskites, serve as unique ionic layer structural motifs for accommodating and transporting interstitial oxygen defects. Crucially, oxide-ion migration proceeds via a previously unrecognized propeller-type interstitialcy mechanism, in which correlated torsional and cage-deformation motions of the Ca/La- and Nb-centered coordination environments dynamically reshape local migration bottlenecks and facilitate successive oxygen-

exchange events. Extension of this concept to close-packed double-perovskite framework further shows that ionic-layer number and connectivity can be modulated to regulate interstitial-oxygen accommodation and transport. Together, these results establish ionic layers as designable structural motifs and identify their number, connectivity, and local flexibility as structural parameters for engineering interstitial-oxygen defect chemistry and transport in close-packed perovskite SEs beyond conventional vacancy-mediated frameworks.

2. Experimental section

2.1 Synthetic method

Polycrystalline $\text{Ca}_{4-x}\text{La}_x\text{Nb}_2\text{O}_{9+0.5x}$ ($0 \leq x \leq 0.2$) and $\text{Ca}_{3-x}\text{La}_x\text{WO}_{6+0.5x}$ ($0 \leq x \leq 0.2$) samples were synthesized by the traditional high-temperature solid-phase reaction method. CaCO_3 (99.99%, Aladdin), Nb_2O_5 (99.99%, Aladdin), WO_3 (99.99%, Aladdin), and La_2O_3 (99.99%, Aladdin) were used as raw materials. Prior to use, La_2O_3 raw material was pre-fired at 950°C for 2 hours to remove absorbed H_2O and CO_2 . For $\text{Ca}_{4-x}\text{La}_x\text{Nb}_2\text{O}_{9+0.5x}$ ($0 \leq x \leq 0.2$) series, stoichiometric amounts of the precursors were weighed, thoroughly ground in an agate mortar with ethanol as a dispersing medium, and dried to obtain a homogeneous mixture. The powders were uniaxially pressed at 300 MPa, calcined, reground, and repelletized. Final sintering was performed in alumina crucibles at 1450°C for 10 h with heating and cooling rates of $5^\circ\text{C}/\text{min}$, yielding dense ceramics with a relative density of $\sim 90\%$. The $\text{Ca}_{3-x}\text{La}_x\text{WO}_{6+0.5x}$ ($0 \leq x \leq 0.2$) series was synthesized using an analogous solid-state route. Stoichiometric amounts of CaCO_3 , La_2O_3 , and WO_3 were thoroughly mixed and ground, followed by calcination at 1000°C for 10 h. The calcined powders were reground and pressed into pellets, which were subsequently sintered in alumina crucibles at 1200°C for 12 h to obtain the final ceramics with a relative density of $\sim 82\%$. The ceramic density was determined from the measured mass and geometric dimensions of the pellet, and the relative density was calculated with respect to the theoretical density derived from the refined crystallographic parameters.

2.2 Characterization methods

The phase purity was examined by powder X-ray diffraction (XRD) using a Panalytical X'Pert PRO diffractometer with Cu K α radiation (40 kV, 40 mA). Variable-temperature XRD patterns were collected on the same instrument equipped with an Anton Paar HTK 1200N high-temperature stage over $25\text{--}1000^\circ\text{C}$. The high-resolution synchrotron X-ray powder diffraction (SPD) data was collected at the BL44B2 ($\lambda = 0.4146909 \text{ \AA}$) beamlines at SPring-8, Japan. High-resolution time-of-flight (TOF) neutron powder diffraction (NPD) data were collected on the BL09: TREND beamline at the China Spallation Neutron Source (CSNS), Dongguan, China. Variable-temperature total scattering neutron pair distribution function (nPDF) data were collected at 300 K, 873 K, and 1073 K on the BL-1B NOMAD beamline at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory. Total scattering X-ray pair distribution function (XPDF) data were collected at the BL13SSW beamline of the Shanghai Synchrotron Radiation Facility (SSRF) and the BL08W beamline of SPring-8, Japan. Average structure refinements on PDF data were

carried out using PDFgui software.⁴⁵ A big-box model (a $10 \times 16 \times 5$ super cell, $\sim 89.11 \text{ \AA} \times 80.08 \text{ \AA} \times 86.6 \text{ \AA}$) was constructed for Reverse Monte Carlo (RMC) simulations of the PDF data for the complex perovskite $\text{Ca}_{4-x}\text{La}_x\text{Nb}_2\text{O}_{9+x/2}$. For double perovskite $\text{Ca}_{3-x}\text{La}_x\text{WO}_{6+x/2}$, a $14 \cdot 14 \cdot 10$ supercell ($\sim 78.45 \text{ \AA} \times 78.68 \text{ \AA} \times 82.23 \text{ \AA}$) was constructed for Reverse Monte Carlo (RMC) simulations. RMC simulations were performed using RMCProfile.⁴⁶ Rietveld refinements of XRD and NPD data were conducted using Topas-Academic⁴⁷ and Jana2006,⁴⁸ respectively.

Morphological characterization and elemental mapping were performed using a scanning electron microscope (SEM300, Zeiss Gemini) equipped with an energy-dispersive spectrometer (Oxford ULTIM MAX 170), and a JEOL-2100F field-emission transmission electron microscope operating at 200 kV with a JED-2300 Si/Li EDX detector. Ultra-soft X-ray absorption (XAS) spectra were collected at the 4B9B beamline of the Beijing Synchrotron Radiation Facility. X-ray photoelectron spectroscopy (XPS) was carried out with monochromatic Al K α radiation (200 W) on an AXIS Supra instrument. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) data were collected on a high-temperature platform 400 simultaneous analyzer (STA 449 F3 Jupiter, NETZSCHGerätëbau GmbH).

AC impedance spectroscopy was performed on a Solartron 1260 frequency response analyzer in the range of 10^{-1} - 10^7 Hz. Pt paste was applied to both sides of the ceramic pellets and sintered at 750°C for 0.5 h to remove organic components and form porous Pt electrodes. Impedance data were analyzed using ZView software.⁴⁹ Oxygen transport number was determined by electromotive force (EMF) measurements using an oxygen concentration cell over 500–1000°C, with one side exposed to pure O₂ ($p\text{O}_2 = 1 \text{ atm}$) and the other to 1% O₂ ($p\text{O}_2 = 10^{-2} \text{ atm}$).

Bond-valence site energy (BVSE) calculations were performed using the SoftBV program,⁵⁰ and low-energy pathways identified in the BVSE maps were used to trace possible oxide-ion migration trajectories. Classical molecular dynamics (MD) simulations were conducted using the DL_POLY code in the NVT ensemble.⁵¹ A $4 \times 10 \times 4$ supercell was constructed for MD simulations, with interatomic interactions modeled. Data were analyzed with the VMD software package.⁵²

Ab initio molecular dynamics (AIMD) simulations were carried out to investigate oxide-ion migration. All calculations were performed using the projector augmented wave (PAW) pseudopotentials⁵³ as implemented in the Vienna ab initio simulation package.⁵⁴ The exchange-correlation interactions were described using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).^{55,56} A plane-wave energy cutoff of 400 eV was applied for both geometry optimizations and AIMD simulations. The Brillouin zone was sampled with a $1 \times 2 \times 1$ k -point mesh centered at the Γ point for all calculations.

3. Results and discussion

3.1 Crystal structure and solid solution of $\text{Ca}_{4-x}\text{La}_x\text{Nb}_2\text{O}_{9+x/2}$.

To experimentally tailor the local structure and enhance the sublattice flexibility of the complex perovskite framework, we introduced La substitution at the Ca site in $\text{Ca}_{3-x}\text{La}_x\text{Nb}_2\text{O}_{9+x/2}$. As shown in Fig. 2a, the XRD patterns of $\text{Ca}_{4-x}\text{La}_x\text{Nb}_2\text{O}_{9+x/2}$ ($0 \leq x \leq 0.2$) indicate the solid solution limit is close to $x = 0.1$, as also revealed by Rietveld analysis of XRD patterns for $x = 0.1$ composition (Figure S1). Beyond this composition ($x > 0.1$), the formation of impurity phase Nb_2O_5 is observed. Rietveld refinement of synchrotron X-ray powder diffraction (SPD) data the $x = 0.1$ composition, using the B-site 1:2 ordered structural model (space group: $P2_1/c$), yields an excellent fit with refinement factors of $R_p = 3.86\%$, $R_{wp} = 5.8\%$, $\text{GOF} = 3.13$ (Fig. 2b, Table S1).

The unit cell parameters systematically increase with La substitution (Fig. 2c), consistent with the slightly larger ionic radius of La^{3+} (1.03 Å) relative to Ca^{2+} (1.00 Å), which drives lattice expansion. Selected electron diffraction patterns and the corresponding high-resolution TEM image (Figs. 2d-f, Figure S2) as well as HAADF-STEM images (Fig. 2g) of $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$ further confirmed the formation of B-site ordered complex perovskite structure. TEM elemental mapping of $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$ (Fig. 2h, Figure S3) demonstrate the uniform distribution of each element (La, Ca, Nb, and O) without elemental segregation. Complementary SEM-EDS mapping of the bulk ceramic (Figure S4) also confirms the uniform distribution of all constituent elements at the macroscopic scale.

3.2 Electrical properties and thermomechanical stability of $\text{Ca}_{4-x}\text{La}_x\text{Nb}_2\text{O}_{9+x/2}$.

The electrical properties and thermal stability of $\text{Ca}_{4-x}\text{La}_x\text{Nb}_2\text{O}_{9+x/2}$ were systematically investigated. For the optimized composition $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$, the complex impedance plot (Fig. 3a) shows distinct contributions from bulk and grain boundary, with characteristic capacitances of $3.75 \cdot 10^{-12}$ F/cm and $1.62 \cdot 10^{-11}$ F/cm, respectively. Compared with the parent composition (Figure S5), the La-doped composition exhibits an additional low-frequency Warburg-type electrode response with a much larger characteristic capacitance of $6.81 \cdot 10^{-5}$ F/cm, which is attributed to interfacial ion diffusion between electrode and electrolyte, indicative of ionic conduction (Supplementary Note 1).⁵⁷ To identify the nature of the mobile charge species, oxygen transport number was measured by the EMF method (Fig. 3b). Within the intermediate temperature range (500–700°C), the transport number exceeds 0.6, unambiguously demonstrating that oxide-ions dominate the conduction mechanism. Arrhenius plots of bulk conductivities for the $\text{Ca}_{4-x}\text{La}_x\text{Nb}_2\text{O}_{9+x/2}$ in air ($0 \leq x \leq 0.15$, Fig. 3c) demonstrate conductivities nearly two orders of magnitude higher than those of the parent $\text{Ca}_4\text{Nb}_2\text{O}_9$, indicating the critical role of La doping in enabling interstitial oxygen defects and enhancing oxide-ion transport.

The total conductivities of $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$ measured over a wide oxygen partial pressure range ($1-10^{-28}$ atm, Fig. 3d) indicate the emergence of an *n*-type electronic contribution under low- $p\text{O}_2$ conditions. This behavior is consistent with the oxygen transport number measurements, where the lower values at high temperatures reflect the onset of *n*-type conduction. Such *n*-type conduction behavior could be rationalized by the donor-doping defect chemistry of La substitution, in which $\text{La}_{\text{Ca}}^\bullet$ donor defects are primarily compensated by introduced interstitial oxygen defects. Under low- $p\text{O}_2$ conditions, the charge-compensation mechanism may partially shift towards electronic compensation, which could involve ionization of interstitial oxygen-related defect states and/or a reduction in interstitial oxygen content. Details of the defect-chemical interpretation are provided in Figure S6 and Supplementary Note 2.

Variable-temperature XRD measurements reveal that $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$ preserves its crystal structure up to 1000°C without any structural transitions or decomposition (Figs. 3f, Figure S7). The thermal expansion coefficients (TECs), derived from the VT-XRD data (Figs. 3g-h), give the axis TECs of $\alpha_a = 1.16 \cdot 10^{-5} \text{ K}^{-1}$, $\alpha_b = 1.7 \times 10^{-5} \text{ K}^{-1}$, $\alpha_c = 5.1 \times 10^{-5} \text{ K}^{-1}$, and volumetric TEC of $\alpha_v = 3.37 \times 10^{-5} \text{ K}^{-1}$, respectively. These values fall within the optimal range for thermal compatibility with fuel cell electrolyte and electrode components.^{58–60} Complementary TG-DSC analysis (Fig. 3i) further confirms excellent phase stability across the full operating window of $25-1000^\circ\text{C}$.

3.3 Structure of $\text{Ca}_{4-x}\text{La}_x\text{Nb}_2\text{O}_{9+x/2}$.

Table 1
Final refined structural parameters of $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$ from NPD data.

Atom	site	x	y	z	Occ.	$U_{\text{iso}}(\text{\AA}^2)$	BVS
Ca1	2a	0.0000	0.0000	0.0000	0.95(3)	0.014(1)	3.02
La1	2a	0.0000	0.0000	0.0000	0.05(3)	0.023(2)	4.23
Ca2	2d	0.5000	0.5000	0.0000	0.97(1)	0.023(2)	3.11
La2	2d	0.5000	0.5000	0.0000	0.03(1)	0.023(2)	4.51
Ca3	4e	0.244(3)	0.502(3)	0.064(1)	0.95(2)	0.025(2)	1.92
La3	4e	0.244(3)	0.502(3)	0.064(1)	0.05(2)	0.025(2)	3.36
Ca4	4e	0.743(2)	0.485(2)	0.266(1)	0.96(1)	0.013(5)	1.88
La4	4e	0.743(2)	0.485(2)	0.266(1)	0.04(1)	0.013(5)	3.25
Ca5	4e	0.750(2)	0.018(3)	0.101(1)	1	0.027(1)	1.89
Nb1	4e	-0.004(2)	0.017(3)	0.3368(9)	1	0.019(6)	4.32
Nb2	4e	0.500(2)	0.005(2)	0.1645(9)	1	0.030(7)	4.05
O1	4e	-0.045(2)	0.187(3)	0.092(1)	1	0.023(9)	1.73
O2	4e	0.448(2)	0.694(2)	0.2197(9)	1	0.016(9)	1.72
O3	4e	0.056(2)	0.768(3)	0.249(1)	1	0.021(6)	1.91
O4	4e	0.565(2)	0.302(2)	0.129(1)	1	0.018(1)	1.97
O5	4e	0.066(2)	0.689(3)	0.094(1)	0.90(4)	0.010(1)	2.17
O6	4e	0.452(2)	0.814(3)	0.0540(1)	1	0.018(1)	1.86
O7	4e	0.244(2)	0.409(2)	0.2633(8)	1	0.011(9)	1.88
O8	4e	0.754(2)	0.608(2)	0.065(1)	1	0.013(1)	1.88
O9	4e	0.262(2)	0.120(3)	0.098(1)	1	0.022(1)	2.00
O _i	4e	0.817(3)	0.575(2)	0.573(5)	0.11 (3)	0.017(3)	2.22

*Space group: $P2_1/c$ (14), $a = 9.8438(4) \text{ \AA}$, $b = 5.5651(1) \text{ \AA}$, $c = 17.3314(5) \text{ \AA}$, $\beta = 125.572(2)^\circ$, $V = 772.26(5) \text{ \AA}^3$, $Z = 4$.

Taking advantage of the high sensitivity of neutron diffraction to oxygen, high-resolution neutron powder diffraction (NPD) was employed to determine the oxygen-defect configuration in $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$. During refinement, La was allowed to occupy both the A-site and B-site Ca positions, with the Ca and La

occupancies at each shared crystallographic site constrained to sum to unity. The refinement indicates that La can be accommodated at both A and B sites for Ca, but with a relatively higher occupancy at the A-site, consistent with Bond-valence-sum (BVS) analysis showing that La BVSs at the A sites are closer to its formal valence, whereas La atoms at the B sites are more overbonded (Table 1). This disordered distribution is also supported by the comparable ionic radii La^{3+} and Ca^{2+} in both coordination environments.

To identify the oxygen defects directly, the high-resolution NPD data were further examined using charge-flipping analysis. A localized residual nuclear-density maximum was resolved at a non-framework position and assigned to an interstitial oxygen site at the 4e Wyckoff position (0.817(3), 0.575(2), 0.573(5)) (Figs. 4a-b). Subsequent DFT-based geometry optimization converged to a chemically reasonable local configuration, further supporting this assignment (Fig. 4c). BVS analysis shows that the main Ca/Nb/O framework is generally consistent with the expected formal valences, whereas the overbonding tendency of La at the B-site Ca positions is consistent with the refined preference for the higher La occupancy at the A-site (Table 1). The oxygen occupancies, particularly at apical sites, were carefully examined by allowing all crystallographic oxygen sites to refine. Most lattice oxygen sites remained essentially fully occupied within the sensitivity of the refinement, whereas a small oxygen deficiency was resolved at the apical O5 site, with a refined occupancy of 0.90(4). This is consistent with the proximity of O5 to the interstitial oxygen position, indicating local oxygen disorder around the interstitial oxygen environment.

To probe the impact of interstitial oxygen species on the electronic structure of $\text{Ca}_{4-x}\text{La}_x\text{Nb}_2\text{O}_{9+x/2}$, O K-edge soft X-ray absorption spectroscopy (XAS) was further performed. The O K-edge XAS spectra (Fig. 4d) display characteristic features associated with transitions into Nb 4d-derived t_{2g} and e_g states, followed by contributions from Ca-3d states. Relative to the parent phase, $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$ exhibits an enhanced t_{2g} -related pre-edge feature, consistent with additional local oxygen coordination around Nb and strengthened Nb-O hybridization.⁶¹ The parent O 1s spectrum contains two lattice-oxygen components at 529.9 and 527.9 eV (Fig. 4e), whereas La substitution introduces a higher-binding-energy component at approximately 531.2 eV for $x = 0.05$ (Fig. 4f). This component increases in intensity and shifts to approximately 533.3 eV for $x = 0.10$ (Figure S8). This evolution of the high-binding-energy component is consistent with the incorporation of interstitial oxygen species, which occupy energetically distinct sites relative to the lattice oxygen.⁶²

Nb K-edge EXAFS measurements further elucidate the local coordination environment variations in $\text{Ca}_{4-x}\text{La}_x\text{Nb}_2\text{O}_{9+x/2}$. For parent $\text{Ca}_4\text{Nb}_2\text{O}_9$, Fourier transform (FT) k^3 -weighted EXAFS spectra were well fitted in both k - and R -space without invoking interstitial oxygen scattering paths (Figures S9a-b), yielding an R -factor of 2.1% (Table S2). In contrast, for composition $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$, inclusion of interstitial oxygen scattering was essential for an accurate fit (Figs. 4g-h), significantly improving the R -factor to 1.2% (Table S3). Wavelet transform (WT) analysis of the EXAFS data provides complementary confirmation, with additional interstitial oxygen scattering feature in $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$ (marked in Fig. 4i) absent in

the parent compound (Figure S9c). Together, these findings unambiguously demonstrate that La substitution drives the incorporation of interstitial oxygen within the $[\text{Ca}'\text{O}_6]$ layer and underpins the enhanced oxide-ionic conductivity observed in $\text{Ca}_{4-x}\text{La}_x\text{Nb}_2\text{O}_{9+x/2}$.

3.4 Correlated disorder and dynamically accessible metastable sites of interstitial oxygen in local structure.

To gain deeper insight into the local structural variations associated with interstitial oxygen incorporation, we performed combined X-ray and neutron pair distribution function (PDF) analysis combined with reverse Monte Carlo (RMC) modeling for $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$. Small-box refinements of both X-ray (Fig. 5a) and neutron (Fig. 5b) PDF data reveal the average structure satisfactorily, but notable discrepancies remain in the short-range region (1–5 Å, marked by red arrows in Figs. 5a-b), indicating the local structural disorder or distortions beyond the average structure of $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$. To address these deviations, large-box RMC simulations were performed using a supercell of $\sim 89.11 \times 80.08 \times 86.60$ Å (Fig. 5c), yielding an excellent refinement to both X-ray and neutron PDF data (Figs. 5d and 5e) and providing a statistically robust real-space description of local structural disorder. Bond valence sum (BVS) analysis of all atomic configurations in the RMC supercell model (Figure S10) shows that the BVS distributions of Ca, La, Nb, and O remain overall centered within chemically reasonable ranges, supporting the chemical plausibility of the RMC-derived local structure.

The RMC-derived atomic configurations provide further support for the presence of interstitial oxygen in the lattice by revealing a statistically well-defined distribution of interstitial oxygen species preferentially residing within the ionic $[\text{Ca}'\text{O}_6]$ layers (Fig. 5f), consistent with the neutron-diffraction-based charge-flipping analysis and subsequent DFT optimization. Statistical analysis of the local coordination environments of interstitial oxygen defects indicates a broad distribution of interstitial-oxygen geometries around B-site Ca' cations (Figs. 5g-l), indicating that the interstitial oxygen adopts not a single rigid coordination geometry, but a dynamically evolving ensemble of multiple metastable local environments. These asymmetric linkages distort the neighboring Ca-O polyhedra and LaO_6 octahedra, generating correlated disorder and dynamically accessible low-energy migration gateways. Such structural motifs in local structure are expected to substantially lower the migration barrier for oxide ion transport, providing a structural basis for the enhanced ionic conductivity.

3.5 Propeller-Type Interstitialcy Oxygen Migration Dynamics.

From a structural-chemistry perspective, the close-packed perovskite framework imposes strong geometrical constraints on local structural motion. Neighboring Nb- and Ca/La-centered coordination environments are geometrically interconnected and possess limited free volume for independent motion. Consequently, torsion of one coordination unit must be accommodated by correlated deformation of adjacent polyhedra and Ca/La-O cages. In this structural sense, the interconnected coordination polyhedra can be viewed as interlocking gear-like units, whereby twisting of one unit

induces a coupled response of its neighbors. These collective torsional, librational and cage-deformation motions dynamically reshape the local oxygen landscape and migration bottlenecks, thereby facilitating successive oxide-ion displacements through the densely packed framework.

We refer to this coupled structural response as a propeller-type migration mechanism to provide a more precise mechanistic description than the broader and comparatively less specific term “cooperative distortion” commonly used for open-framework ion conductors.^{21,63} Here, “propeller-type” does not imply rigid-body rotation of an isolated polyhedron, but rather a spatially correlated sequence of angular distortions involving multiple geometrically interlocked coordination units. This structural mechanism is further supported experimentally by the predominance of tangential oxygen displacements from variable-temperature neutron PDF combined with RMC analysis and dynamically by the time-resolved coupling between oxide-ion displacement and local framework torsion revealed by AIMD simulations.

To experimentally examine the local structural signatures associated with the proposed propeller-type mechanism, variable-temperature neutron PDF measurements were collected for $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$ at 300 K, 873 K and 1073 K and analysed using complementary small-box refinements and big-box RMC modeling (Fig. 6, Figures S11-13, Tables S4-6 and Supplementary Note 3). The neutron PDF data (Figures S11a-b) show progressive broadening in the low- r region with increasing temperature, indicating an increasing spread of local bond-length distributions. Consistently, the folded RMC configurations reveal a progressively more diffuse oxygen distribution at elevated temperature, whereas the cation sublattices remain comparatively less broadened (Figs. 6a-c). Quantitative displacement distributions and root-mean-square (RMS) displacements extracted from the RMC configurations show that oxygen exhibits the largest temperature-dependent displacement, followed by Ca and then Nb (Figs. 6d-f and Figure S13). This trend indicates enhanced oxygen disorder and substantial flexibility of the Ca-containing ionic layer relative to the more rigid Nb-centered framework.

To further characterize the nature of this structural response, the oxygen displacements were decomposed into radial and tangential components relative to the local M-O directions (Figure S14). The tangential-to-radial displacement ratio, $R_{\text{tan/rad}}$, remains above unity around both Ca/La and Nb, increasing from 1.51 to 1.55 and from 1.97 to 2.04, respectively, between 873 and 1073 K. Consistently, the fraction of tangential-dominated oxygen displacements increases from 69.2% to 70.6% around Ca/La and from 78.4% to 79.9% around Nb. This directional preference is also reflected in the average-structure refinements, which reveal increasingly anisotropic oxygen displacement ellipsoids upon heating from 300 to 1073 K, with their principal axes oriented predominantly transverse to the local M-O bonds (Figure S12). These average- and local-structure results demonstrate a pronounced non-radial character of the high-temperature oxygen dynamics, with a particularly strong tangential component around Nb, indicating that the local structural response is dominated by torsional/librational distortions rather than simple M-O bond stretching. This experimentally observed directional character provides quantitative structural support for the proposed propeller-type dynamics.

To establish the time-dependent relationship between the local structural distortions identified by VT-PDF/RMC analysis and long-range oxide-ion transport, we further performed ab initio molecular dynamics (AIMD) simulations for $\text{Ca}_{4-x}\text{La}_x\text{Nb}_2\text{O}_{9+x/2}$. Unlike the parent $\text{Ca}_4\text{Nb}_2\text{O}_9$, in which all atoms exhibit only lattice vibrations (Figure S15), the mean-square displacement (MSD) analysis (Fig. 7a) reveals that oxide ions exhibit substantial long-range migration, while the Ca, La and Nb sublattices remain essentially immobile. Additional AIMD simulations at multiple temperatures (Figure S16) show a systematic increase in oxide-ion MSD with temperature, indicating progressively enhanced oxide-ion mobility. The oxide-ion diffusion coefficients were then extracted from the linear regime of the MSD curves and their Arrhenius plot of the oxide-ion diffusion coefficients (Fig. 7b) demonstrates an activation energy of 0.63 eV, consistent with low-barrier 2D migration pathways predicted by BVSE calculations (Figure S17, Supplementary Note 4).

Direction-resolved MSD analysis reveals moderate anisotropy of oxide-ion diffusion, with the *a*- and *c*-axis components generally exceeding the *b*-axis component over the 0-100 ps AIMD trajectories (Figure S18), consistent with a preferential in-plane contribution to oxygen motion within the Ca/La-containing layers. Analysis of the AIMD trajectories reveals that long-range transport involves multiple oxide-ions rather than repeated hopping of a single isolated interstitial species (Figure S19). Successive displacement and rearrangement of neighboring framework oxygens indicate an interstitialcy-type exchange process initiated by the interstitial defect. Consistent with this multiple oxide-ion transport mechanism, AIMD scatter plots show pronounced oxygen delocalization, whereas the cation sublattices remain relatively confined (Fig. 7c-d). The evolution of representative local coordination environments around the mobile oxygen species further reveals stepwise changes in oxygen coordination during migration (Figs. 7e-g), demonstrating that long-range transport proceeds through a dynamically evolving sequence of metastable configurations.

Together with the variable-temperature PDF/RMC-derived oxygen displacement distributions (Fig. 7h-j), these AIMD trajectories provide complementary evidence for spatially broadened and dynamically connected oxygen motion at elevated temperature (Fig. 7d bottom). The corresponding local oxygen-displacement distributions around Ca- and Nb-centered environments (Figs. 7k-l) further reveal the non-radial structural response associated with cooperative polyhedral distortions, providing experimental structural support for the proposed propeller-type migration mechanism.

The local NbO_6 torsional dynamics become strongly activated with increasing temperature: the mean rotational/torsional amplitude increases from approximately 23° at 1273 K to 31° at 1473 K and 82° at 1673 K, while the corresponding maximum amplitude increases from approximately 45° to 63° and 129° , respectively (Figure S20a). These results demonstrate pronounced thermal activation of the angular degrees of freedom of the Nb-centered coordination environment. More importantly, the time-resolved AIMD trajectories show that long-range oxide-ion displacement develops within dynamically active intervals in which NbO_6 torsion and neighboring Ca-O and La-O cage deformations evolve concurrently (Figure S20b-c). The relationship is not one of strict instantaneous synchronization between an oxygen coordinate and the rotation of a single polyhedron (Figure S20d). Rather, oxide-ion migration occurs

within a persistently fluctuating framework in which correlated torsional, librational and cage-deformation motions continuously reshape the local oxygen coordination landscape and generate transient configurations favorable for migration.

The cooperative nature of this framework response is further quantified by frame-by-frame correlation analysis. Positive correlations are observed between NbO_6 torsion and both La-O and Ca-O cage torsion at all examined temperatures, with Pearson correlation coefficients of $r = 0.89$ and 0.84 at 1273 K , 0.71 and 0.69 at 1473 K , and 0.92 and 0.88 at 1673 K , respectively (Figure S21). The particularly strong correlations at 1673 K coincide with the largest NbO_6 torsional amplitudes, demonstrating that the enhanced angular motion at elevated temperature is accompanied by increasingly correlated rearrangement of neighboring coordination environments.

Because oxide-ion migration proceeds through the Ca/La-containing layers, we also evaluated possible La-associated trapping from the AIMD trajectories (Figures S22-S26). The most mobile oxygen ions repeatedly enter and leave the first La coordination shell rather than remaining permanently bound, indicating that La provides only transient local stabilization rather than deep trapping. This weak anchoring preserves long-range oxygen mobility within the Ca/La-containing layers.

Taken together, these AIMD results provide the dynamic basis for the propeller-type interstitialcy oxide-ion migration mechanism. The interconnected Nb- and Ca/La-centered coordination units behave as dynamically coupled, gear-like structural units, in which torsional motion of one local environment induces a coordinated response of its neighbors, as visualized in Supplementary Video 1. Their collective angular deformation transiently reshapes migration bottlenecks and facilitates successive oxygen-exchange events through the close-packed framework. This time-dependent description provides the dynamic counterpart to the predominantly tangential oxygen displacements identified experimentally by VT-PDF/RMC analysis, and is further consistent with the BVSE calculations (Figure S17 and Supplementary Note 4) and classical MD simulations (Figures S27-S35, Tables S7-S9 and Supplementary Note 5).

The lower oxide-ion conductivity of the present complex perovskite, relative to well-established RP conductors such as Pr_2NiO_4 - and La_2NiO_4 -based oxides, most likely reflects the more constrained transport topology of the close-packed framework. In RP systems, oxygen hyperstoichiometry is an intrinsic structural feature,⁶⁴ allowing a relatively high concentration of interstitial oxide ions to be accommodated and transported through comparatively continuous two-dimensional pathways. By contrast, in the present material, interstitial oxygen is introduced only through aliovalent La substitution and the solid-solution range remains limited. Moreover, long-range migration does not occur within a pre-existing layered fast-ion network, but instead proceeds through a bottleneck-limited propeller-type interstitial mechanism. In this mechanism, oxide-ion migration is assisted by cooperative distortions of the flexible $[\text{Ca}'\text{O}_6]$ ionic layers around the rigid NbO_6 framework. Comparison with the RP oxychloride system⁶⁵ further highlights the importance of structural openness and free volume, suggesting that the

compact Ca-Nb oxide framework could restrict the absolute concentration of mobile carriers relative to more open RP-type structures.

Beyond the specific Ca-Nb chemistry explored here, the Ca-W double-perovskite illustrates how the ionic-layer concept can be developed from a structural descriptor into an engineering principle for defect accommodation and ion transport in close-packed perovskite-derived frameworks (Supplementary Note 6). Relative to the complex-perovskite architecture (Figure S36a), the double-perovskite framework (Figure S36b) increases the number of ion-containing layers within the structural repeat from one to two and enhances their connectivity, thereby expanding the configurational space available for interstitial-oxygen accommodation and local structural rearrangement. High-resolution NPD directly identifies an additional interstitial oxygen site (Figures S37-38 and Tables S10-11), while PDF/RMC analysis reveals a heterogeneous ensemble of three- to five-coordinate Ca/La/W environments around the defect (Figures S39). Consistent with this expanded structural flexibility, the La-substituted Ca-W phase exhibits predominantly oxide-ion conduction and a conductivity more than one order of magnitude higher than that of the Ca-Nb complex perovskite (Figures S40). Computational analyses (Figure S41-45) further show that long-range oxygen transport remains dynamically coupled to correlated WO_6 and Ca/La-O framework torsion, exhibiting the similar underlying propeller-type interstitialcy character despite the distinct crystallographic architecture.

These observations shift the design emphasis from transferring a specific composition or mechanism to engineering the ionic-layer architecture itself. Ionic-layer number, connectivity, flexibility and local chemistry emerge as coupled structural variables that modulate interstitial-oxygen accommodation and the cooperative framework dynamics required for transport. This architecture-based strategy links crystallographic topology, defect accommodation and propeller-type migration, providing a structural route to interstitial oxide-ion transport beyond conventional vacancy-mediated frameworks.

4. Conclusions

In summary, inspired by the rock-salt layers of classical RP structures, we identify an ionic-layer engineering principle for enabling interstitialcy oxide-ion transport in close-packed perovskite framework. In the B-site ordered complex perovskite $\text{Ca}_{3-x}\text{La}_x\text{Ca}'\text{Nb}''_2\text{O}_{9+x/2}$, La substitution introduces interstitial oxygen defects that preferentially accommodated within the ionic $[\text{Ca}'\text{O}_6]$ layers, resembling the R-P rock-salt layers. These defects generate dynamically accessible metastable coordination environments and migrate through a propeller-type interstitialcy process, in which correlated torsional and cage-deformation motions of interconnected Ca/La- and Nb-centered coordination units transiently reshape migration bottlenecks and facilitate successive oxygen-exchange events. Extension to the Ca-W double-perovskite architecture further demonstrates that increasing ionic-layer number and connectivity could expand the configurational space for interstitial-oxygen accommodation while retaining similar propeller-type migration dynamics, with the La-substituted Ca-W phase exhibiting oxide-ion conductivity more than one order of magnitude higher than that of the Ca-Nb complex perovskite. These results identify ionic-layer number, connectivity, flexibility and local chemistry as designable structural variables

linking crystallographic topology, defect accommodation and propeller-type migration, providing an architecture-based route to interstitial oxide-ion conduction beyond conventional vacancy-mediated frameworks. More broadly, this ionic-layer perspective provides a structural framework for defect engineering in perovskite-related functional materials in which oxygen stoichiometry and local structural dynamics govern functionality.

Declarations

COMPETING INTERESTS

The authors declare no competing interests.

AUTHOR CONTRIBUTIONS

X.J.K. and X.H.L. conceived and supervised the project and prepared and revised the manuscript. Y.Z. carried out the syntheses, characterization of samples, and data analysis. C.L. helped collect the neutron pair distribution function data. Z.H.T. and P.M. helped collect the neutron diffraction data. Q.L.G., K.L., J.L.S., and X.R.X. provided thoughtful and constructive comments on this manuscript. All authors reviewed and

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DATA AVAILABILITY

The authors declare that all data supporting the findings of this study are available within the paper or supplementary information files.

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Figures

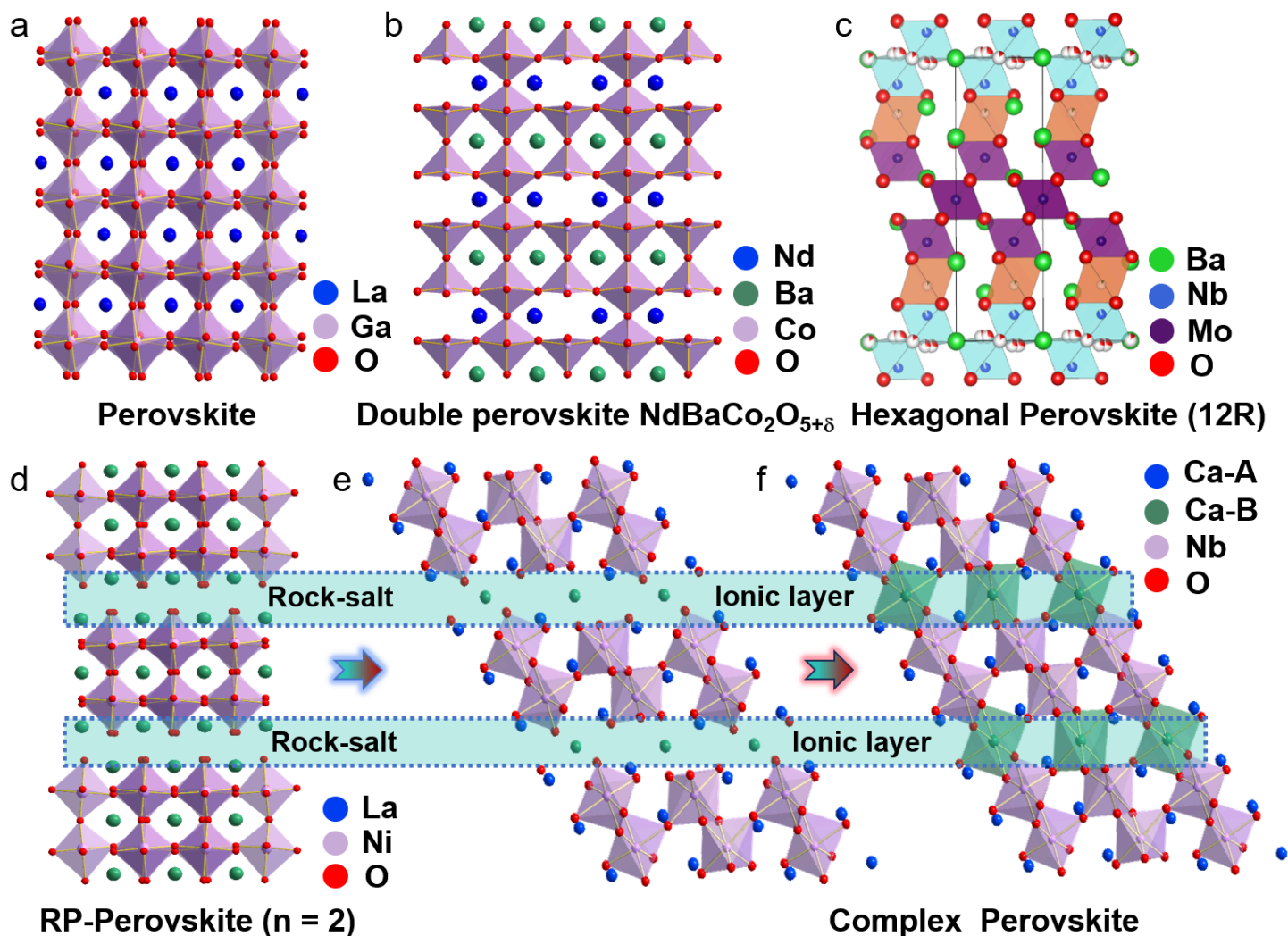


Figure 1

Crystal structures of representative perovskite-based solid electrolytes. (a) Conventional ABO_3 perovskite $LaGaO_3$. (b) Double perovskite $NbBaCo_2O_{5+d}$ ($d = 0.5$). (c) Hexagonal perovskite derived polymorph $Ba_7Nb_{3.9}Mo_{1.1}O_{20.05}$. (d) Ruddlesden-Popper La_2NiO_4 . (e-f) B-site ordered complex perovskite $Ca_3CaNb_2O_9$, in which highly coordinated alkaline-earth Ca cations occupy both the A and B $\tilde{c}$ sites.

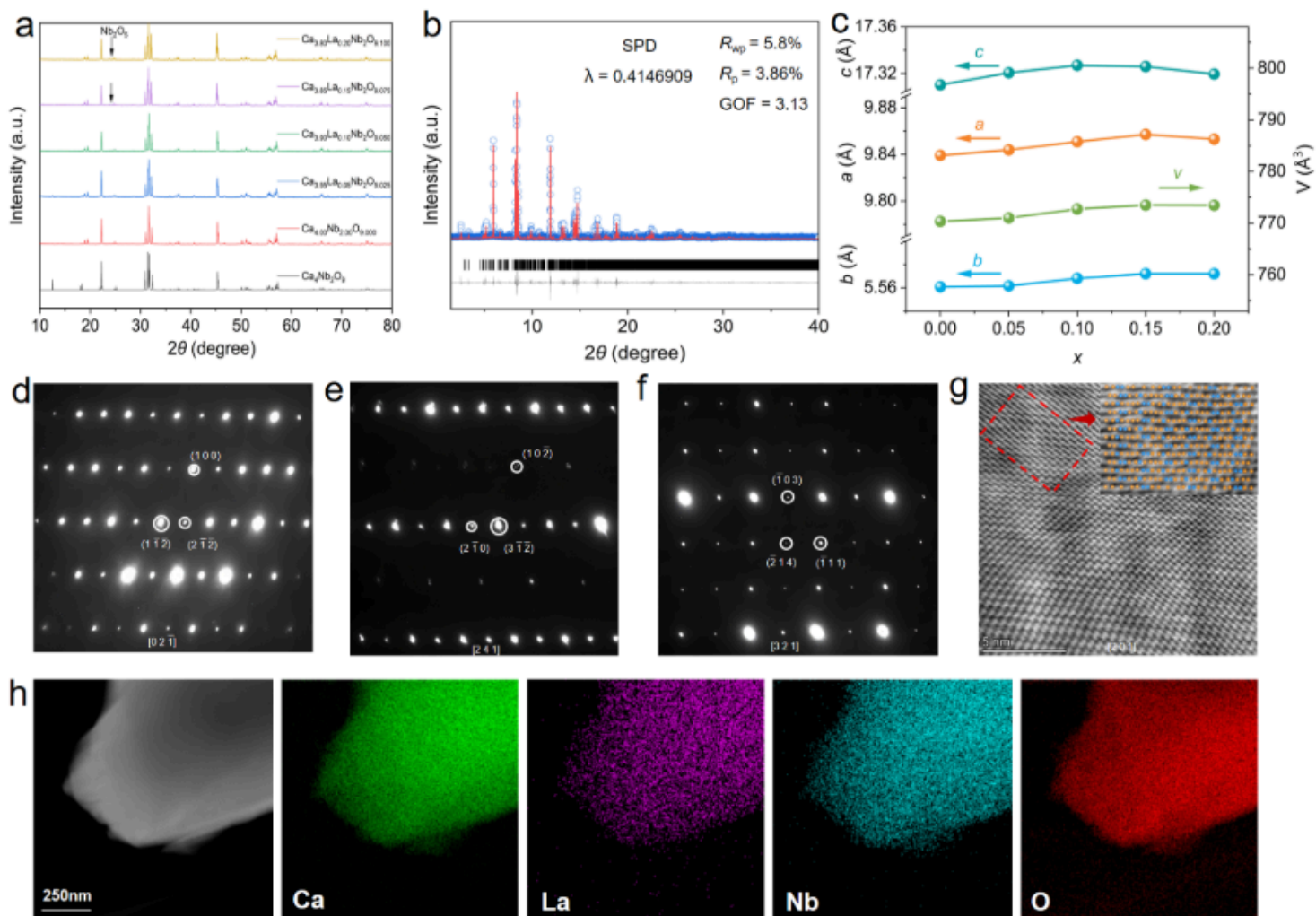


Figure 2

Structure and solid solution behavior of $\text{Ca}_{4-x}\text{La}_x\text{Nb}_2\text{O}_{9+x/2}$. (a) XRD patterns of compositions with $0 \leq x \leq 0.2$. (b) Rietveld refinement of SPD data for $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$. (c) Refined lattice parameters as a function of La content x . (d-f) Electron diffraction patterns viewed along (d) [02], (e) [241], (f) [321] direction, respectively. (g) HADDF-STEM image viewed along [201] direction, and the inset shows a magnified atomic-resolution image corresponding to the ordered complex perovskite structure. (h) TEM images and corresponding elemental mapping of $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$.

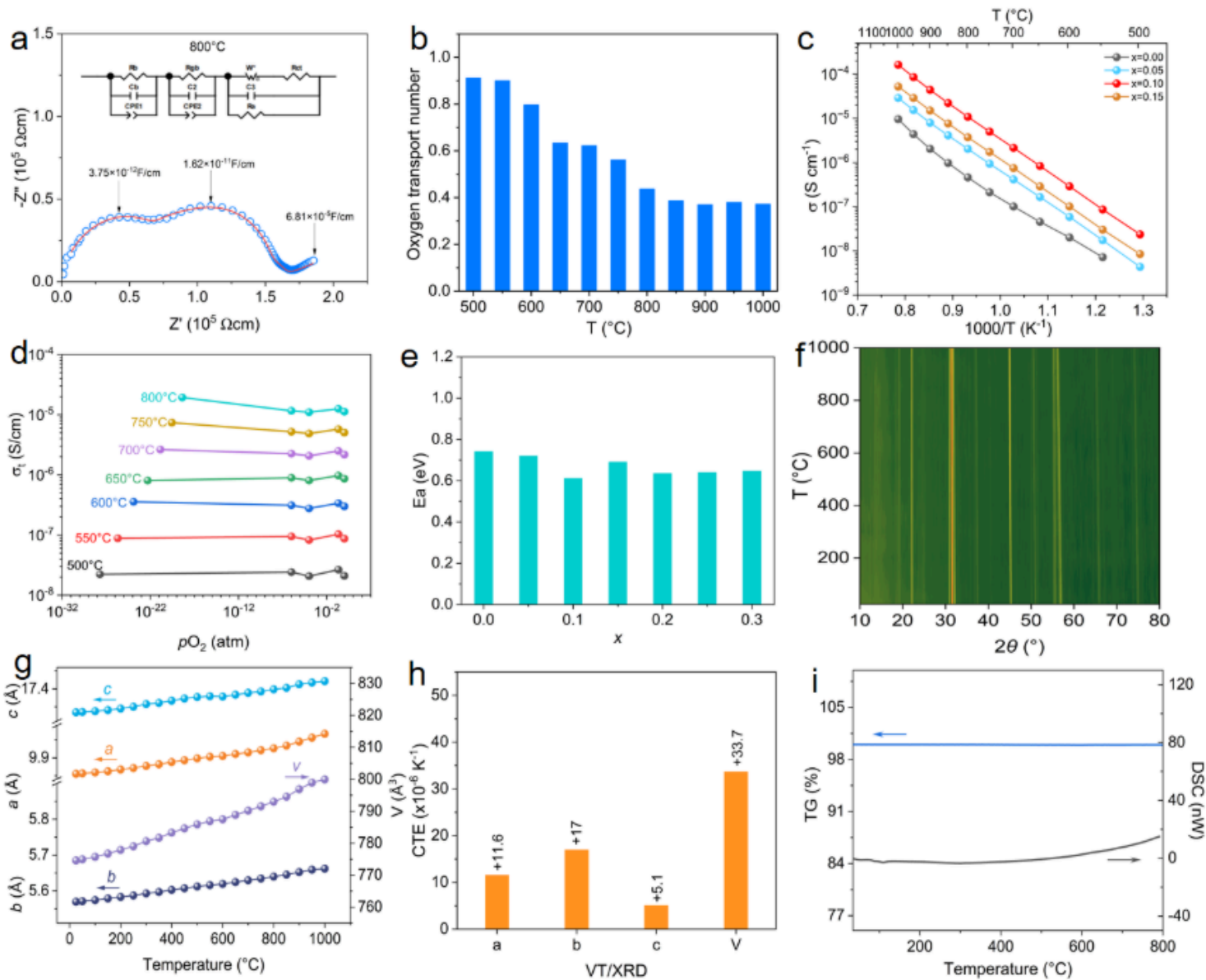


Figure 3

Electrical properties and thermal stability of $\text{Ca}_{4-x}\text{La}_x\text{Nb}_2\text{O}_{9+x/2}$. (a) Complex impedance plots of $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$ at 800°C with the equivalent circuit used for fitting. (b) Oxygen transport number of $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$. (c) Bulk conductivities for compositions $0 \leq x \leq 0.15$ in air. (d) Conductivities of $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$ under oxygen partial pressures from 1 to 10^{-28} atm. (e) Activation energies for compositions $0 \leq x \leq 0.3$. (f) VT-XRD patterns of $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$. (g) Thermal evolution of lattice parameters, (h) Thermal expansion coefficients derived from VT-XRD. (i) TG-DSC curves of $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$.

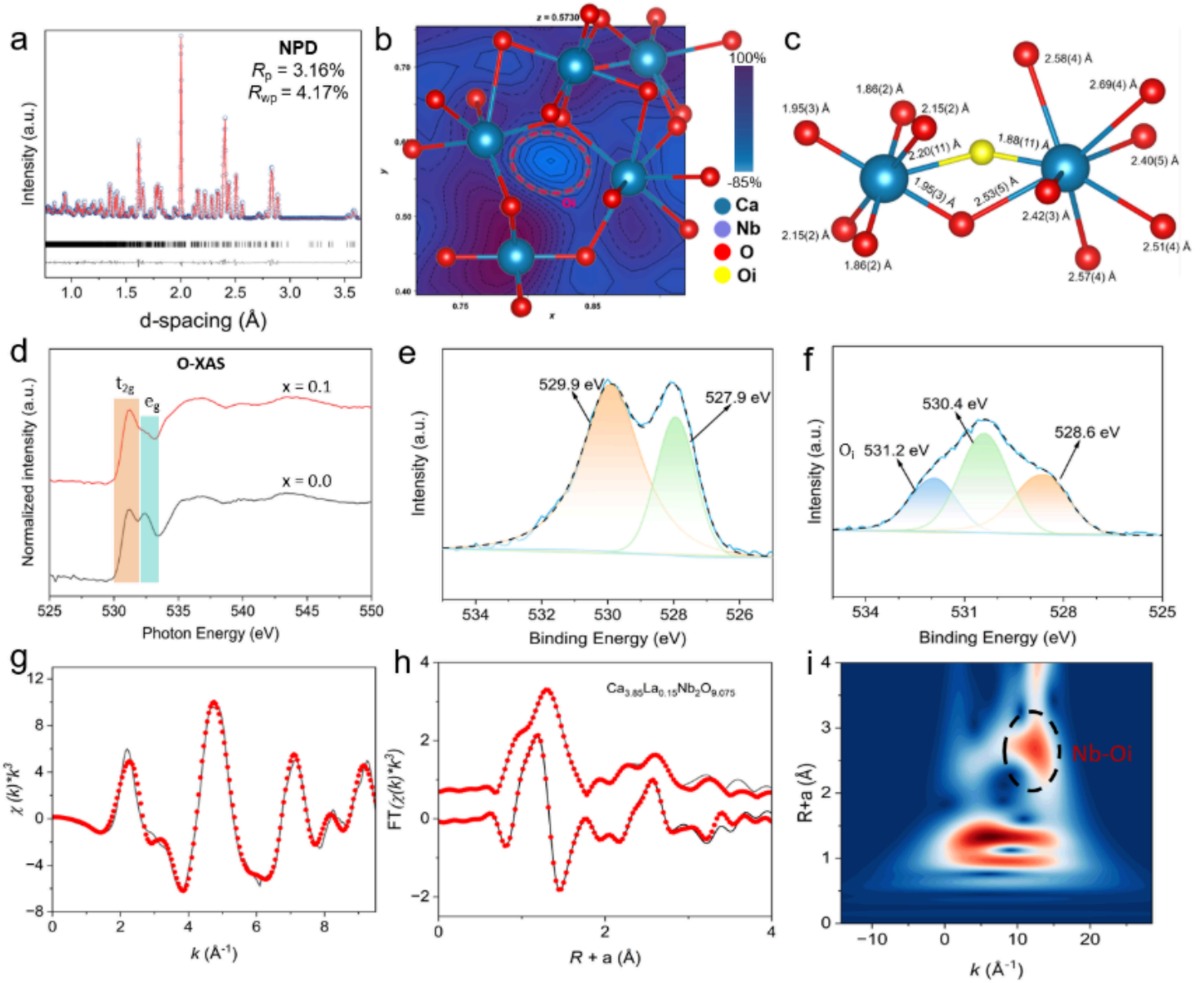


Figure 4

Average and local structural analysis of $\text{Ca}_{4-x}\text{La}_x\text{Nb}_2\text{O}_{9+x/2}$. (a) Rietveld refinement plots of NPD data for $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$. (b) Difference nuclear density map from NPD data, with the red dashed circle highlighting residual nuclear density assigned to an interstitial oxygen site. (c) Coordination environments of the interstitial oxygen site. (d) Oxygen K-edge soft X-ray absorption spectra for $x = 0$ and $x = 0.1$ compositions. (e-f) O-1s XPS fine spectra of $\text{Ca}_{4-x}\text{La}_x\text{Nb}_2\text{O}_{9+x/2}$ with (e) $x = 0$ and (f) $x = 0.05$. (g, h) Nb K-edge EXAFS spectra (line) and curve fitting (points) in k^3 -weighted (g) k -space and (h) R -space. (i) Wavelet transform of Nb K-edge EXAFS spectra.

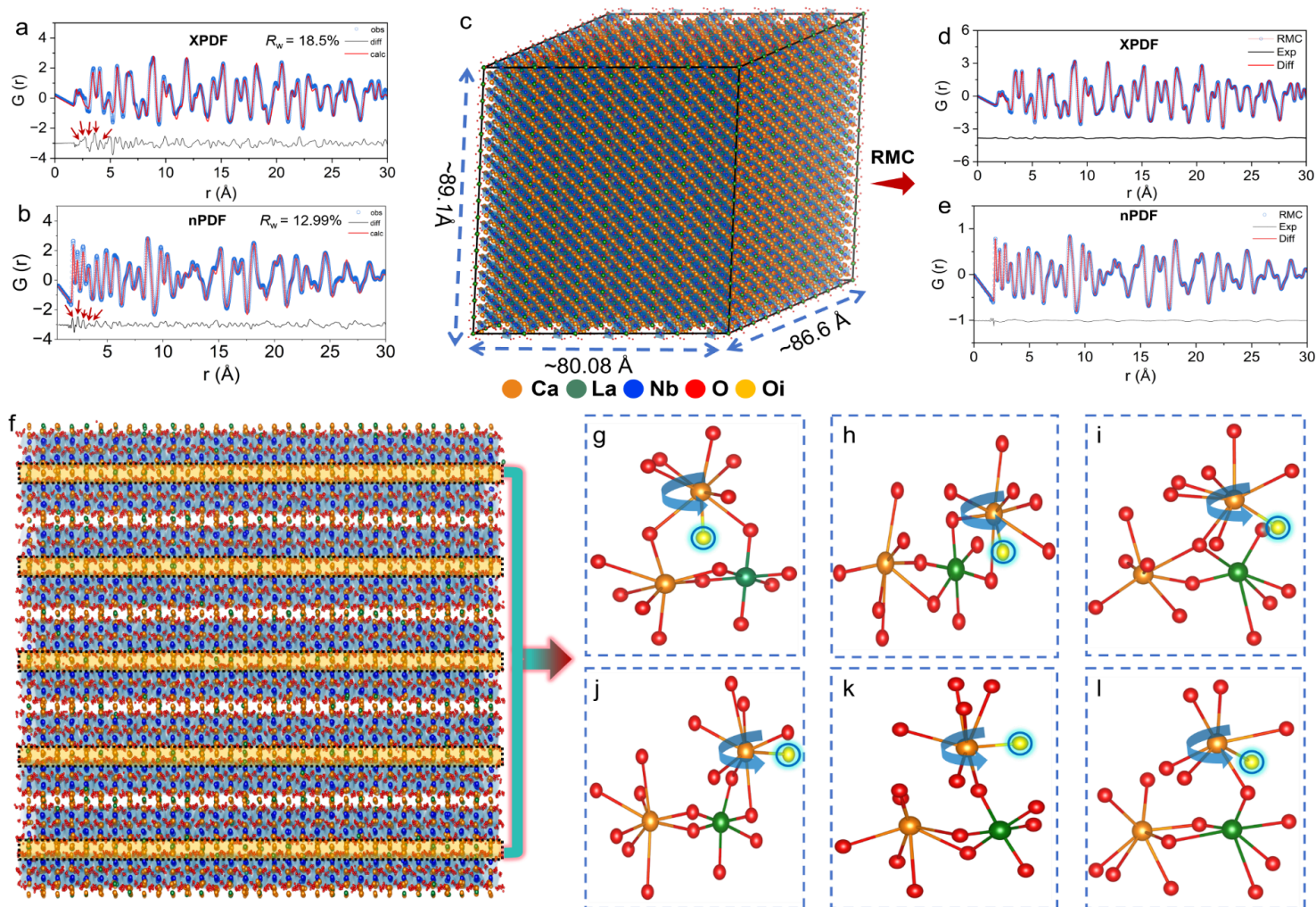


Figure 5

Local structure of $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$ revealed by X-ray and neutron PDF analysis with RMC modeling.

(a, b) Small-box refinements of (a) X-ray PDF and (b) neutron PDF data. (c) Three-dimensional atomic configuration of the supercell ($\sim 89.11 \times 80.08 \times 86.60 \text{ \AA}$) used for RMC simulations. (d, e) Big-box refinements of (d) X-ray and (e) neutron PDF data. (f-l) RMC-derived local coordination environments of interstitial oxygens, where arrows indicate dynamically evolving interstitial-oxygen coordination geometries.

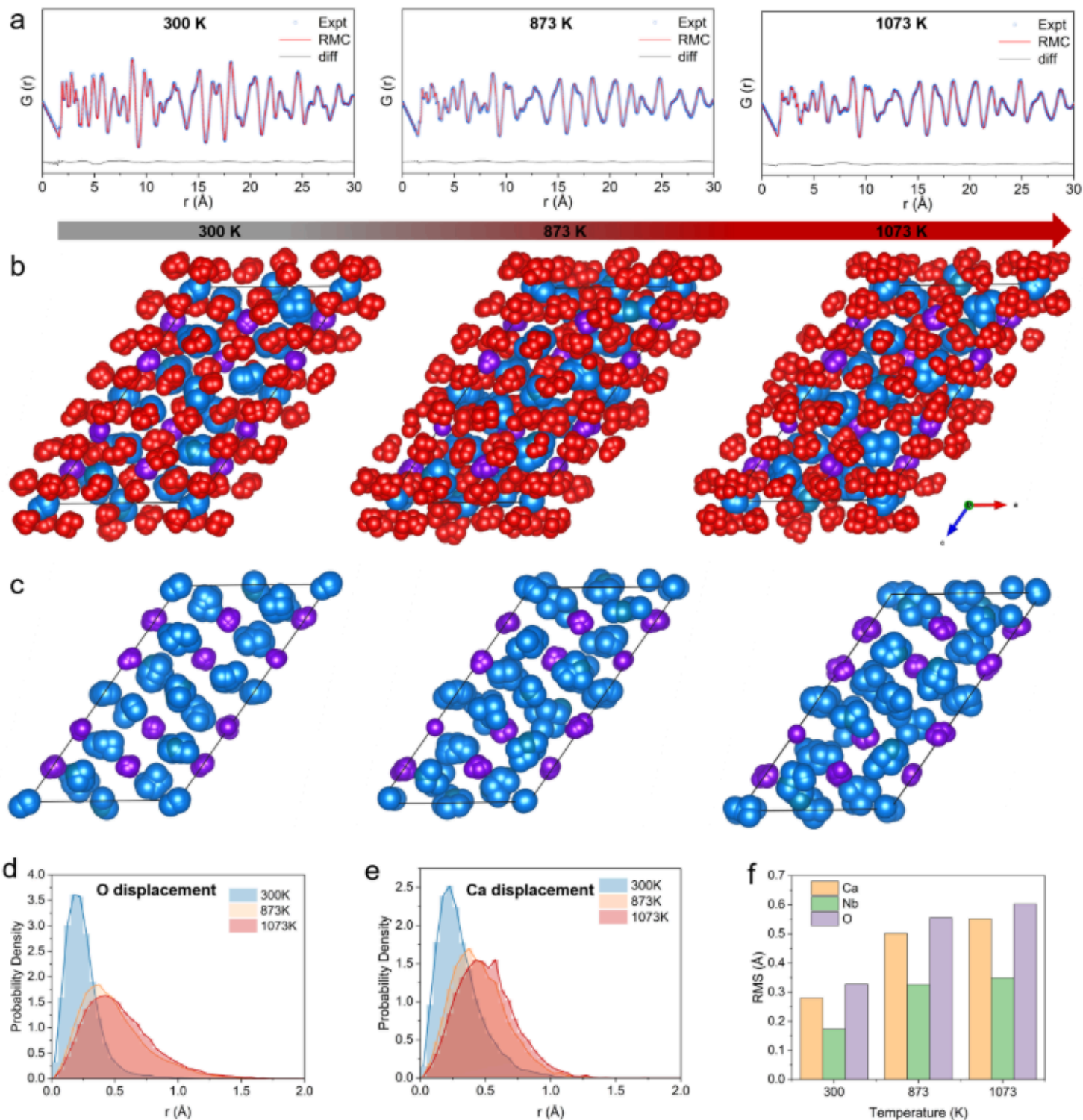


Figure 6

Variable-temperature neutron PDF data combined with RMC analysis for $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$. (a) Big-box refinements of the neutron PDF data collected at 300 K, 873 K, and 1073 K, respectively. (b, c) Folded RMC-refined atomic configurations at 300 K, 873 K, and 1073 K, obtained by folding the $10 \times 16 \times 5$ RMC supercell back into the primitive $P1$ unit cell. (b) Full folded atomic configurations. (c) Corresponding cation sublattice. Purple, blue and red spheres represent Nb, Ca/La and O atoms, respectively. (d, e)

Displacement distributions of (d) O and (e) Ca atoms extracted from the RMC configurations. (f) RMS displacements of Ca, Nb and O atoms as a function of temperature.

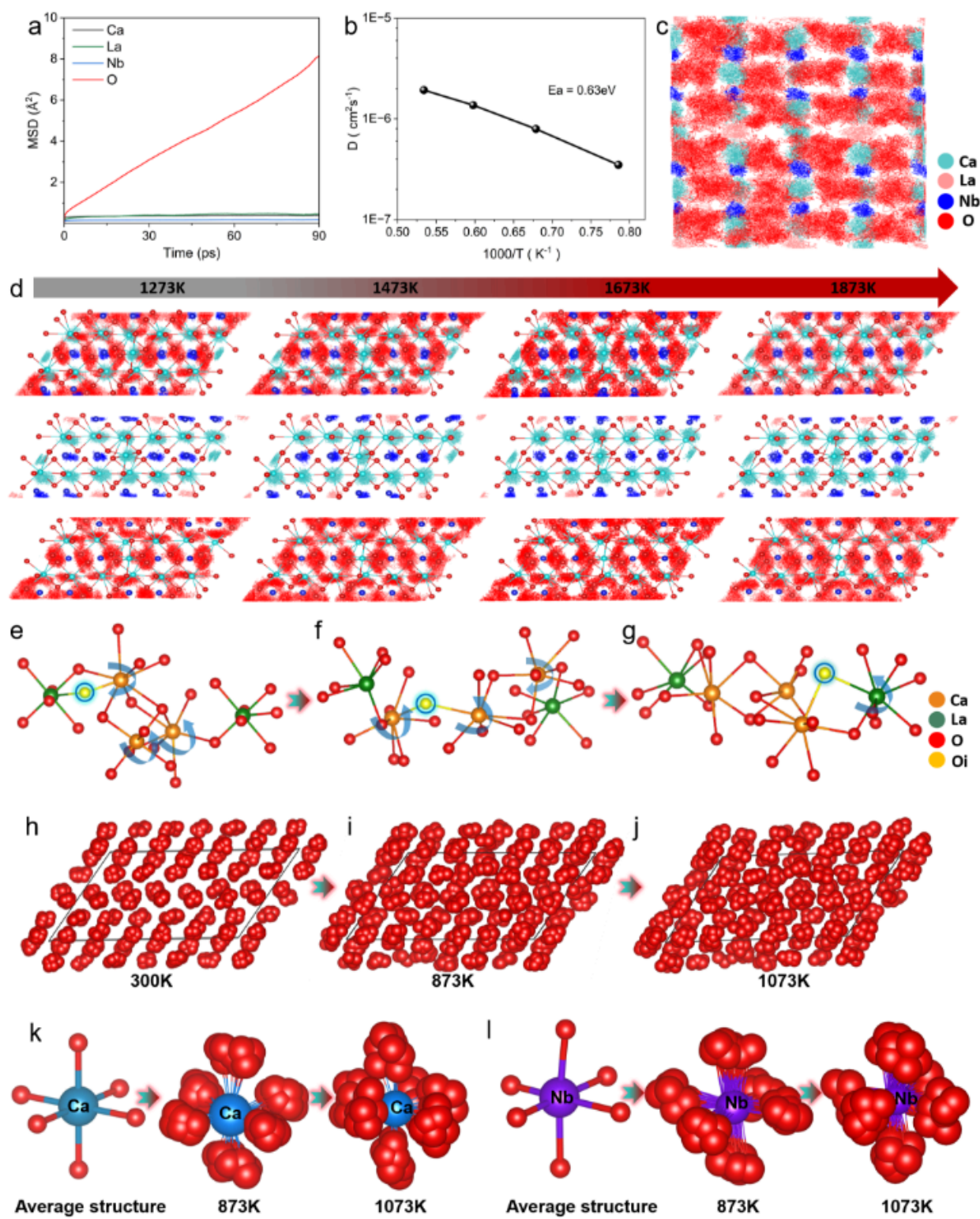


Figure 7

AIMD simulations and variable-temperature PDF combined with RMC analysis of oxide ion migration in $\text{Ca}_{3.9}\text{La}_{0.1}\text{Nb}_2\text{O}_{9.05}$. (a-g) AIMD simulation results. (a) Mean square displacements of Ca, La, Nb, and O

atoms at 1673 K. (b) Arrhenius plot of the oxide-ion diffusion coefficients. (c) Scatter plots of cations and oxide ions. (d) Time- and temperature-dependent scatter plots from AIMD trajectories along the [010] direction, showing (top) all atoms, (middle) cations, and (bottom) oxide-ion trajectories. (e-g) AIMD-derived local coordination environments around interstitial oxygens as a function of simulation time, illustrating the evolution of long-range migration pathways. (h-l) Variable-temperature PDF data analyzed by RMC modeling. (h-j) Folded RMC-derived oxygen configurations at (h) 300 K, (i) 873 K, and (j) 1073 K. For visualization, each $10 \times 16 \times 5$ RMC supercell was folded back into the primitive *P1* unit cell. (k, l) Oxygen-atom displacement distributions around representative (k) Ca- and (l) Nb-centered coordination environments in the folded RMC configurations at elevated temperatures, compared with the corresponding average-structure oxygen sites.

Supplementary Files

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