

Strain-Enhanced Low-Temperature High Ionic Conductivity in Perovskite Nanopillar-Array Films

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ABSTRACT: Solid oxide ionic conductors with high ionic conductivity are highly desired for oxide-based electrochemical and energy devices, such as solid oxide fuel cells. However, achieving high ionic conductivity at low temperatures, particularly for practical out-of-plane transport applications, remains a challenge. In this study, leveraging the emergent interphase strain methodology, we achieve an exceptional lowtemperature out-of-plane ionic conductivity in Na_{0.5}Bi_{0.5}TiO₃ (NBT)-MgO nanopillar-array films. This ionic conductivity (0.003 S cm⁻¹ at 400 °C) is over one order of magnitude higher than that of the pure NBT films and surpasses all conventional intermediate-temperature



ionic conductors. Combining atomic-scale electron microscopy studies and first-principles calculations, we attribute this enhanced conductivity to the well-defined periodic alignment of NBT and MgO nanopillars, where the interphase tensile strain reaches as large as +2%. This strain expands the *c*-lattice and weakens the oxygen bonding, reducing oxygen vacancy formation and migration energy. Moreover, the interphase strain greatly enhances the stability of NBT up to 600 $^{\circ}$ C, well above the bulk transition temperature of 320 $^{\circ}$ C. On this basis, we clarify the oxygen migration path and establish an unambiguous strain-structure-ionic conductivity relationship. Our results demonstrate new possibilities for designing applicable high-performance ionic conductors through strain engineering.

INTRODUCTION

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With the advancement of clean energy and environmental technologies, such as solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs), oxide ionic conductors gained increasing attention due to the growing demand for efficient oxygen ion transport to enhance device performance, particularly near room temperature.¹⁻⁴ Consequently, developing solid oxide ionic conductors with enhanced ionic conductivity at reduced operating temperatures down to a more cost-effective range (<400 °C) has been a central objective.^{5,6} Despite substantial research efforts devoted, this goal remains elusive due to the high activation and migration energy of oxygen at low temperatures in existing systems.^{7–9} In this regard, doped-perovskite systems, which can accommodate a wide range of cations to effectively modulate the oxygen bonding strength and facilitate its formation and migration, have emerged as promising candidates for ionic conductors.¹⁰⁻¹³ For example, magnesium-doped $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) can exhibit competitive ionic conductivity (~0.01 S cm⁻¹ at 600 °C) and stability, positioning it as a viable alternative to commercially used yttria-stabilized zirconia.^{14,15} However, its low-temperature performance remains insufficient for practical applications. The limited development of lowtemperature, high-performance systems, combined with the constraints in current methodologies for developing new systems, continues to pose significant challenges in meeting practical application requirements.¹⁶⁻¹⁸

Among the various developed strategies, strain modulation represents a prominent approach for enhancing ionic conductivity.^{19–23} Typical methods include chemical strain through doping,^{10,24} lateral interfacial strain via lattice mismatch in multilayer thin films,²⁵⁻²⁷ vertical strain in vertically aligned nanocomposite (VAN) films, 28-30 and the interphase strain method.^{31,32} Chemical doping typically can introduce local chemical strain due to the difference in ion radius between the dopant and host lattice.³³ Additionally, it can facilitate the formation of oxygen vacancy when the dopant has a different valence, making it an effective way for regulating ionic conductivity, as seen in examples such as RE₂O₃-doped CeO₂ electrolytes.³⁴ However, challenges in controlling local strain magnitude, maintaining material homogeneity, and suppressing the generation of impurity phase limit its broader application.^{7,35} For the interfacial strain method, leveraging the clamping effects from the substrate regarding lattice parameter and symmetry,^{19,36} it offers advantages in stabilizing metastable high-conducting phase to achieve superior performance. For

Received:	September 11, 2024
Revised:	November 19, 2024
Accepted:	November 20, 2024





Figure 1. Structural characterization of the NBT-MgO nanopillar-array films. (a) Schematic of the SOFC device based on nanopillar-array films. (b) XRD spectra for pure NBT film and NBT-MgO nanopillar-array film on the (001)-orientated STO substrate. (c) Synchrotron-based reciprocal space mapping (RSM) studies around the STO substrate (103) diffraction for pure NBT film (left) the NBT-MgO film (right), where H and L represent the (h00) and (00l) Miller indices, respectively. (d) Surface topography of the NBT-MgO nanopillar-array film. (e) Cross-sectional STEM image and corresponding EDXS elemental mapping of Mg, Bi, and Ti elements.

example, the δ -Bi₂O₃ phase, known for its high conductivity but typically unstable in bulk form, can be stabilized in the Bi₂O₃/YSZ superlattice thin film through the mismatch strain.^{37,38} Since interfacial strain is two-dimensional, this method excels in controlling the in-plane (IP) conductivity. However, it faces challenges in regulating out-of-plane (OOP) conductivity, which is often required by devices like SOFCs (Figure 1a), as well as issues related to strain relaxation along the OOP direction and the limited availability of substrates that can introduce suitable mismatch strain.^{39–41} In this regard, films engineered by the vertical strain and featuring a VAN structure have emerged as a promising configuration, offering outstanding performance that allows high strain tunability up to micrometer thickness and enabling a fast OOP ionconducting channel.^{42,43} For example, the OOP ionic conductivity of the SrZrO₃-RE₂O₃ nanopillar can be tuned and enhanced through tensile strain.⁴⁴ In this configuration, the key lies in controlling the two different phases to form uniformly and periodically aligned nanopillars, which can significantly enhance macroscopic performance but which remains quite challenging. This difficulty arises because the configuration of the two phases depends on a delicate balance of various energies, including the relative stability of the phases, interfacial energies, elastic energies, surface energies, and more.45

In this study, using the interphase strain method, we achieved superior ionic conductivity in a model perovskite ionconducting system NBT by introducing vertical strain through a simple binary oxide MgO. The ionic conductivity realized in these NBT-MgO nanopillar-array films reaches up to 0.003 S cm⁻¹ at 400 °C, which is over one order of magnitude higher than that of the pure NBT films and surpasses the performance of the entire family of intermediate-temperature ionic conductors. Moreover, such conductivity demonstrates robust stability even at temperatures up to 600 °C. This exceptional performance is attributed to the well-defined periodic alignment of NBT and MgO nanopillars and the periodic tensile strain (up to 2%), as confirmed by our atomic-scale electron microscopy investigations, achieved through precise control of the nucleation and growth of the two phases. First-principles calculations reveal that in this configuration, NBT features larger unit-cell volumes and octahedral distortions, which effectively decrease migration energy barriers of oxygen ions and create a set of low-energy migration pathways. This study not only introduces a new superior ionic conductor with strong application potential but, more importantly, provides valuable insights into the rational design of a wide range of highperformance ionic conductors.

RESULTS AND DISCUSSION

NBT-MgO nanopillar-array films were grown on (001)oriented SrTiO₃ (STO) substrates using pulsed laser deposition (PLD). The resulting $(001)_{pc}$ -oriented nanopillar arrays (with pc referring to pseudocubic indices) exhibited highly crystalline NBT and MgO phases, without any impurity phases detected (Figure 1b). Reciprocal space mapping (RSM) study around the (103) plane of the pure NBT film (left panel in Figure 1c) confirmed that the single NBT phase was fully strained on the substrate, with an IP lattice parameter identical to that of the substrate (3.90 Å) and an OOP lattice parameter identical to that of the NBT bulk of 3.88 Å. Upon introducing the MgO second phase, the c-axial lattice spacing of the NBT phase expanded significantly (orange spectra in Figure 1b), corresponding to nearly 2% OOP tensile strain (right panel in Figure 1c). Given the low solubility of Mg in NBT (typically below 2%) and the negligible strain associated with



Figure 2. Ionic conductivity of the NBT-MgO nanopillar-array films. (a) Impedance spectra (Nyquist plots) of the pure NBT film and NBT-MgO nanopillar-array film at 400 °C. (b) Comparison of the ionic conductivity of the NBT-MgO nanopillar-array film with those reported in previous studies.^{5,14,16,18,29,43} Red solid circles represent the intrinsic properties of the strained NBT phase (excluding the MgO phase and normalized to the NBT phase). Red dashed circles indicate the ionic conductivity of the entire NBT-MgO film (including the MgO phase). (c) Temperature dependence of the OOP XRD spectra for the NBT-MgO nanopillar-array film. The red dashed line indicates the phase transition temperature, which is significantly higher than that of pure-phase NBT at 320 °C (white dashed line). (d) Oxygen partial pressure (pO_2) dependence of the ionic conductivity for the NBT-MgO film, including measurements in air, inert (N_2) atmosphere, and reducing (H_2/Ar) atmosphere at 450 °C.

substituting Ti⁴⁺ with six-coordinated Mg²⁺ ions,^{15,46} such a tensile strain in NBT is primarily attributed to the coherent NBT-MgO interface formed in the thin film (discussed in detail in Figure 3). A subsequent phi-scan indicated a fourfold IP symmetry of the NBT phase and a cube-on-cube epitaxial relationship (Figure S1). The spatial assembly of the NBT and MgO phases was further examined using atomic force microscopy and advanced scanning transmission electron microscopy (STEM). In contrast to the smooth surface topography in single-phase NBT films (Figure S2), the NBT-MgO nanopillar-array film displayed a checkerboard-like surface topography, with NBT nanopillars embedded in the MgO matrix (Figure 1d). Cross-sectional STEM imaging and corresponding energy-dispersive X-ray spectroscopy (EDXS) elemental mapping (Figure 1e) further revealed that the NBT (purple) and MgO (orange) phases featured a nanopillar (~20 nm) configuration with a sharp interface and arranged in an alternative distribution with long-range periodicity in the lateral direction. Additionally, the selected area electron diffraction (SAED) pattern of the NBT-MgO nanopillararray film further clarified the matching relationship between the NBT and MgO phases as well as the STO substrate (Figure S3). Such a periodic nanopillar configuration, along with the coherent interfaces between the two phases, benefits strain interactions at interfaces, preventing strain relaxation up

to hundreds of nanometers along the OOP direction. This ensures effective long-range modulation of the OOP ionic conductivity of the NBT phase.

The ionic conductivity (σ) of the NBT-MgO nanopillararray films was characterized using AC impedance spectroscopy measurements.⁴⁷⁻⁴⁹ A top-down OOP transport configuration was used for the measurements (Figure S4a). Figure 2a compares the typical complex impedance plots of the NBT-MgO nanopillar-array film with those of a single-phase NBT film. The single-phase NBT film, with inferior ionic conductivity, displays a large arc in the high-frequency range (purple line in Figure 2a), which can be effectively modeled using a resistor (R) and capacitor (C) in parallel (Figure S4b). In contrast, due to the introduced tensile strain, a significant reduction in resistance ($R_{\rm film}$, extracted from the highfrequency arc) was observed in the NBT-MgO nanopillararray film. The frequency-dependent resistance data were then converted into frequency-dependent conductivity using the formula $\sigma = L/RS$ (where R_{film} is the resistance of the thin film, S is the area of the top Pt electrode, and L is the film thickness). The extracted ionic conductivity of the single-phase NBT film is close to the NBT bulk (Figure 2b), which is around 9×10^{-5} S cm⁻¹ at 400 °C. This not only confirms the high quality of the film but also excludes the possible contribution from the NBT-STO interfacial strain to the



Figure 3. Atomic-scale characterization of the NBT-MgO nanopillar-array films. (a) HAADF-STEM image of the NBT-MgO interface. Right-side enlarged images from the purple- and orange-shaded regions show the unit cells of the strained NBT and MgO, respectively. (b) Intensity profiles of atomic columns extracted from the red (parallel to the interface, top panel), blue (on the interface, middle panel), cyan (parallel to the interface, bottom panel) dashed rectangle-frame regions in (a). (c) Color-mapped c/a ratio of the NBT phase overlaid on the same region in (a). (d) Schematic structural model and Bi–Bi–Ti triangle bottleneck for the tensile strain-engineered NBT phase. (e) Ti *L*-edge XAS of pure NBT and the NBT-MgO nanopillar-array film. Note that I_{eg} and I_{t2g} indicate the peak intensity of e_g and t_{2g} , respectively. (f) Schematic of the strain-induced evolution of the Ti–O hybridization and corresponding orbital configurations.

ionic conductivity. In comparison, the NBT-MgO nanopillararray film exhibits a significantly increased ionic conductivity up to 0.003 S cm⁻¹ at 400 °C. Figure 2b compares this ionic conductivity achieved in our nanopillar-array films with previously reported values for typical ion conductors. Remarkably, the NBT-MgO nanopillar-array film shows over an order of magnitude increase in ionic conductivity compared to the bulk NBT and surpasses that of classic intermediatetemperature ionic conductors, highlighting the critical role of interphase tensile strain. Notably, unlike the single-phase NBT film, which undergoes a phase transition at low temperatures of 320 °C (indicated by a kink in the σ -*T* plot) and shows a slow increase in ionic conductivity with temperature, the NBT-MgO nanopillar-array film demonstrates robust stability and a significant enhancement in ionic conductivity with rising temperature. Specifically, the rate of change in ionic conductivity with temperature (the inverse slope of the plot in Figure 2b) essentially corresponds to the activation energy of oxygen vacancies (E_a) . We quantified the E_a values for both the single-phase NBT film and the NBT-MgO nanopillar-array film. At 400 °C, the E_a for the NBT-MgO nanopillar-array film $(\sim 0.65 \text{ eV})$, modulated by interphase strain, is significantly lower than that of the single-phase NBT film (~0.81 eV). Moreover, it is worth mentioning that such superior ionic conductivity (0.003 S cm⁻¹ at 400 °C) exceeds the minimum conductivity requirement for a 1 μ m electrolyte in SOFCs,^{1,5} which demonstrates strong potential to significantly reduce the working temperature of SOFCs to a low-temperature region (<400 °C). The temperature-dependent XRD results in Figure

2c further confirmed the thermal robustness of the NBT-MgO nanopillar-array film, demonstrating high stability up to 600 °C, which is significantly higher than that of the pure NBT with a phase transition around 320 °C. To rule out potential contributions from electronic conducting, direct current (DC) conductivity measurements were performed using the same electrode configuration as in alternating current (AC) measurements. The electronic contribution was found to be negligible, being over two orders of magnitude lower than the ionic conductivity (Figure S5). Furthermore, the nearly identical ionic conductivity under different oxygen partial pressures further confirmed the oxide ionic conductivity nature of the thin film (Figure 2d). Under normal or oxidizing conditions, single-phase NBT is a pure oxide ionic conductor with negligible electronic conduction.¹⁴ In reducing atmospheres, slight *n*-type conduction may occur, but only when anion nonstoichiometry, due to oxygen loss, and the partial reduction of Ti⁴⁺ to Ti³⁺ are present.¹⁴ However, this is absent in our NBT-MgO thin film, as evidenced by our conductivity measurements under inert (N_2) and reducing (H_2/Ar) atmospheres. This stability is attributed not only to the film's high crystallinity and low defect concentration, aided by the coherent NBT-MgO interfaces, but also to the effective mediation by energy band alignment and the built-in electric field (BIEF) at the interface.⁵⁰⁻⁵² The BIEF effectively suppresses electron movement while promoting ionic migration, further highlighting both the advantages of the NBT-MgO heterostructure design from an electronic structure



Figure 4. DFT calculations on the origin of strain-enhanced ionic conductivity in NBT-MgO nanopillar-array films. (a) Supercell models for the NBT-MgO interface (top panel) and single-strained NBT phase (bottom panel), respectively. (b) Comparison of the system energies for different oxygen vacancy configurations. (c) Calculated energy profiles for oxygen migration along IP (top panel) and OOP (bottom panel) directions. (d) Oxygen ion migration energy as a function of OOP strain along different directions in the NBT.

perspective and the critical role of BIEF in the development of high-performance ionic conductors.⁵¹

To obtain further insights into the superior ionic conductivity observed in NBT-MgO nanopillar-array films, we conducted a quantitative analysis of atomic-scale structural distortion using spherical aberration-corrected STEM. The atomically resolved HAADF-STEM images (Figure 3a) show a typical atomically sharp and coherent NBT-MgO interface in the nanopillar-array film. For the Z-contrast HAADF-STEM image, the atomic intensity is proportional to the $Z^{1.7}$ (Z is the atomic number).⁵³ Combining the analysis of the intensity of the atomic column (Figure 3b) with simulated STEM images (Figure S6), we can confirm that the left and right nanopillars in the image correspond to the [100] zone axis NBT phase and the [100] zone axis MgO phase, respectively. We then fitted the atomic positions and calculated the c/a ratios of the NBT lattice to probe the structural distortions of the NBT phase. As expected, all the NBT unit cells exhibit strong tetragonal distortion, with c/a ratios larger than unity (Figure 3c), which is consistent with the XRD results. Notably, the entire NBT nanopillar is fully strained and uniformly elongated (Figure S7), including regions near and away from both the NBT-MgO interfaces (IP direction) and the NBT film-substrate interfaces (OOP direction). This underscores the advantages of the interphase strain method in uniformly modulating the strain state, particularly in the OOP direction. Thus, the significantly enhanced ionic conductivity observed can be well attributed to this increased *c*-directional lattice spacing in NBT,

which provides an enlarged migration channel (Bi-Bi-Ti triangle bottleneck) for oxygen ions (Figure 3d).

We next quantified such structural distortion-mediated changes in the oxygen environment in the NBT phase, which is intrinsically decisive in the ionic conductivity of the material. To this end, we collected Ti L-edge X-ray absorption spectroscopy (XAS) of the NBT-MgO nanopillar-array films (Figure 3e). Compared to the pure NBT film, the Ti L-edge XAS of the NBT-MgO nanopillar-array film exhibits a lowenergy shift of the e_g orbital (0.2 eV) and a decreased split energy (Δ_2), indicating an elongated TiO₆ octahedron (Figure 3f). This OOP elongation that creates large spacing facilitates the movements of O atoms along the c-axis, resulting in elevated OOP *c*-axis orbitals $(d_{3z^2-r^2} \text{ and } d_{yz}, d_{zx})$ and lowered IP orbital $(d_{x^2-y^2}$ and $d_{xy})$. Notably, the increased relative intensity of the e_g to t_{2g} orbital (I_{eg}/I_{t2g} from 1.35 to 1.45) in the NBT-MgO nanopillar-array film (Figure 3e) suggests weakened hybridization between Ti and O, further promoting the formation of oxygen vacancy. Note that the energy required to drive oxygen movement within the lattice primarily comprises the formation energy of the oxygen vacancy $(E_{\rm f})$ and the migration energy of the oxygen ion (E_m) . In this sense, these interphase strain-induced alterations in the local structures that can decrease both $E_{\rm f}$ and $E_{\rm m}$ by increasing the oxygen migration space and decreasing the oxygen bonding strength essentially establish a fundamental structural basis and synergistic promote the enhancement of ionic conductivity.

Building on the understanding of strain-tuned structural evolution, the strain-microstructure-ionic transport property relationship was further established with the help of firstprinciples density functional theory (DFT) calculations. We first constructed the NBT-MgO interface model (top panel in Figure 4a) and determined the most favorable formation positions for oxygen vacancies. We calculated and compared the system energies for various oxygen vacancy configurations, including the ones with oxygen vacancy located within the NBT phase, at the NBT-MgO interface, and within the inner MgO phase. Our results indicate that oxygen vacancies are more likely to form in the uniformly stretched NBT phase rather than at the NBT-MgO interface or within the MgO phase (Figure 4b). This finding rationally excludes the possible contributions to ionic conductivity from the MgO phase. We then examined the long-range ion migration paths along both OOP and IP directions (bottom panel in Figure 4a) to elucidate the preferential ion migration paths. The strain-free NBT phase exhibits relatively high and direction-independent oxygen migration energy (~0.82 eV) (Figure 4c), which is consistent with the experimental observations (0.81 eV). Given the A-site chemical complicates of the NBT phase,⁵⁴ we selected two relatively high-energy paths to assess the strain dependence of oxygen migration. With the increase in OOP tensile strain in the NBT phase, an evident decrease in oxygen vacancy migration energy was observed (Figure 4d), indicating that tensile strain positively contributes to the enhancement in ionic conductivity. It is noteworthy that, under a 2% tensile strain, the OOP oxygen vacancy migration energy effectively decreased to around 0.67 eV, closely matching experimental results (0.65 eV). Furthermore, through modifications to the atomic-scale local structural changes, including variations in lattice spacings and orbital configurations, interphase strain mediates local electronic distortions, as shown in Figure 3f. These distortions promote band bending and facilitate the establishment of a BIEF at the NBT-MgO interface (Figures S8 and S9). This effect further suppresses the electronic conduction while enhancing ionic conduction.55,56 These results suggest that by carefully constructing appropriate interphases to precisely fine-tune the local strain state, it is possible to significantly enhance ionic conductivity. The developed interphase strain-engineering approach of strategically combining the two components within a nanopillar-array film presents exciting new possibilities for the advancement of high-performance ionic conductors.

CONCLUSIONS

In this study, through the interphase strain method, we have achieved exceptional (0.003 S cm⁻¹ at 400 °C) and robust (up to 600 °C) ionic conductivity in well-assembled NBT-MgO nanopillar-array films. Notably, this ionic conductivity is primarily along the OOP direction, which is conducive to practical applications, and surpasses that of all conventional intermediate-temperature ionic conductors. Combining advanced electron microscopy and XAS studies, we revealed that the large interphase tensile strain (2%) between the NBT and MgO nanopillars can significantly elongate the lattice and introduce the distortion of oxygen octahedra of the NBT phase, thereby lowering the formation energy of oxygen vacancies and the migration energy of oxygen ions. By integrating these findings with DFT calculations, we elucidated the intrinsic relationship between lattice strain, microstructure, and oxygen migration behaviors. Our work not only clarifies the underlying mechanisms of strain-tuned ionic conductivity but also opens new avenues for the design and development of high-performance ionic conductors.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c12625.

Experimental details for thin film growth, structural characterizations, electron microscopy characterizations, electrical measurements, XAS measurements, and DFT calculation (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant Nos. 22235002 and 22375015), the Outstanding Young Scientist Program of Beijing Colleges and Universities (JWZQ20240101015), the National Key R&D Program of China (Grant No. 2021YFA1202100), the open research fund of Songshan Lake Materials Laboratory (Grant No. 2022SLABFK02), and the open research fund of Guangxi Key Laboratory of Information Materials (Grant No. 221031-K). This research used the resources of the Beijing National Center for Electron Microscopy at Tsinghua University, the Shanghai Synchrotron Radiation Facility (BL02U2 beamlines, China), and the Beijing Synchrotron Radiation Facility (1W1A and 4B9B beamlines, China) of the Chinese Academy of Science.

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