

Strong phonon scattering and enhanced thermoelectric performance in SrTiO₃ polycrystals by simultaneous hydrogen substitution and oxygen vacancy formation

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ABSTRACT: Reduction of lattice thermal conductivity (κ_{lat}) is one of the most critical strategies for achieving high thermoelectric energy conversion efficiency (ZT). SrTiO_3 is regarded as an environmentally benign thermoelectric material. Complex cation-site defects in SrTiO_3 , such as those produced by heavy-mass rare-earth cation substitution and the formation of Sr vacancies, have been proven effective in reducing κ_{lat} . In this paper, we synthesized $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\text{O}\delta}$ bulk polycrystals with complex anion-site defects, incorporating large amounts of both hydrogen anions (H^-) and oxygen vacancies (V_{O}), with the total concentration of $x + \delta$ controlled over a wide range from 0.13 to 0.40. As increasing $x + \delta$ values, κ_{lat} at 300 K largely decreased from 8.22 W/(mK) for pure SrTiO_3 to 4.02 W/(mK) for $\text{SrTiO}_{2.60}\text{H}_{0.27}\text{V}_{\text{O}0.13}$. Both H and V_{O} were found to contribute almost equally to phonon scattering, attributed to local structure distortions in Ti-O_6 octahedra. In contrast, while the carrier activation rate of H^- was nearly 100%, that of V_{O} was only 23–27% in $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\text{O}\delta}$ bulks, allowing the realization of low κ_{lat} and a high power factor (PF) even at high $x + \delta$ values. The highest ZT value of ~ 0.1 was obtained at 300 K for $\text{SrTiO}_{2.87}\text{H}_{0.06}\text{V}_{\text{O}0.07}$, and further increased to 0.21 at 673 K for $\text{SrTiO}_{2.73}\text{H}_{0.16}\text{V}_{\text{O}0.11}$. These findings demonstrate that anion-site defect engineering via mixed-anion substitution and vacancy formation is a promising strategy for further reducing κ_{lat} and enhancing the performance of thermoelectric oxides.

KEYWORDS. Thermoelectric material; Transition metal oxide; Hydrogen; Phonon transport; Carrier transport

1. INTRODUCTION

Thermoelectric effect, that enables direct and reversible conversion between thermal and electrical energy, has been expected to provide a viable route for power generation from waste heat.¹⁻³ The efficiency of thermoelectric energy conversion of the thermoelectric materials is defined by the dimensionless figure of merit, $ZT = S^2 \cdot \sigma \cdot T \cdot \kappa^{-1}$, where S is the Seebeck coefficient, σ is the electronic conductivity, T is the absolute temperature, κ is the sum of electronic (κ_{ele}) and lattice thermal conductivities (κ_{lat}).⁴⁻⁶ Therefore, the large S and high σ (leads to the high power factor, $PF = S^2 \sigma$) coupled with the low κ are required for high ZT . The high ZT has been demonstrated mainly in heavy metal chalcogenides, such as Bi_2Te_3 , PbTe , and GeTe ,^{4,7-9} due to their intrinsic low κ_{lat} . However, the use of toxic elements, such as Pb and Te, is not preferred for wide applications of thermoelectricity. Recently, various effective strategies for reducing κ_{lat} have been proposed for the development of eco-friendly thermoelectric materials, including point defect engineering, nano-structuring, and introduction of local bonding heterogeneity.¹⁰⁻¹²

A perovskite-type oxide SrTiO_3 has been regarded as one of the potential candidates for environmentally benign thermoelectric materials due to their earth abundance, nontoxic nature, and high chemical stability.¹³⁻¹⁵ SrTiO_3 is an n-type semiconductor with the bandgap of ~ 3.2 eV. The aliovalent cation substitution, such as La^{3+} for the Sr^{2+} site and Nb^{5+} for the Ti^{4+} site can increase its σ value by the large increase of carrier concentration.¹⁶ Moreover, the triple degeneracy of the conduction bands formed by Ti $3d$ t_{2g} orbitals and its large electron effective mass $6-8 m_e$ ¹⁵ lead to a large S even at high carrier concentrations. Owing to the promising electronic transport characteristic, the electron-doped SrTiO_3 single crystal possesses high $PF = 20-30 \mu\text{W}/(\text{cmK}^2)$, comparable to that of Bi_2Te_3 at room temperature (RT).¹³⁻¹⁵ However, ZT of the electron-doped SrTiO_3 has been limited to as low as $0.05-0.08$ at RT in single crystals because of its high κ_{lat}

value of ~ 10 W/(mK),¹⁷ which is 10 times higher than ~ 1 W/(mK) of Bi_2Te_3 at RT.¹⁸ To date, most efforts to reduce κ_{lat} in SrTiO_3 have focused on cation-site defect engineering. For example, cation-site defects have been introduced by substituting heavy rare-earth cations and creating Sr cation vacancies, and the double substitution of rare-earth and transition metal cations at the Sr and the Ti sites, respectively.¹⁹⁻²³

On the other hand, we have recently proposed a new approach to reduce κ_{lat} and demonstrated ZT enhancement in SrTiO_3 bulk polycrystal by hydrogen anion (H^-) substitution at the oxygen ion (O^{2-}) sites, i.e., $\text{SrTiO}_{3-x}\text{H}_x$.²⁴⁻²⁶ Heavy-mass element substitution has been a conventional approach to reduce κ_{lat} , while we showed that the substitution of light-mass H^- at the O^{2-} site is very effective to reduce κ_{lat} of SrTiO_3 . Only the 1.9% addition of H^- at the O^{2-} site reduces κ_{lat} from 8 W/(mK) of SrTiO_3 to 6.5 W/(mK) at $x = 0.057$ and further reduces it to 3.6 W/(mK) at maximum $x = 0.216$ for $\text{SrTiO}_{3-x}\text{H}_x$ at RT. The H^- substitution introduces distorted local coordination structures in the $\text{Ti}-(\text{O},\text{H})_6$ octahedra due to the heterogeneity of chemical bonding structures with the weak $\text{Ti}-\text{H}$ bonds and the strong $\text{Ti}-\text{O}$ bonds, which strongly enhances the phonon scattering in the $\text{SrTiO}_{3-x}\text{H}_x$.²⁴ Note that a recent study has demonstrated that isotope substitution of O^{16} with O^{18} in SrTiO_3 effectively reduces the κ_{lat} by nearly 20%, due to mass-difference-induced phonon scattering.²⁷ In addition, H^- substitution generates high carrier concentrations and achieves high carrier mobility with much less grain boundary (GB) scattering than the conventional La-doped SrTiO_3 polycrystals. The H^- substitution does not form a GB potential barrier and thus suppresses electron scattering despite their polycrystalline nature. As a result, $\text{SrTiO}_{3-x}\text{H}_x$ bulk polycrystals exhibit a high PF comparable to the La-doped SrTiO_3 single crystal.²⁵ As a consequence, the $\text{SrTiO}_{3-x}\text{H}_x$ bulk with optimal $x = 0.068$ exhibits a $ZT = 0.11$ at

RT and the ZT value increases continuously up to 0.22 at $T = 657$ K. It is possible to reduce κ_{lat} by increasing x in $\text{SrTiO}_{3-x}\text{H}_x$, but the PF reaches its maximum at low x (i.e., low carrier concentrations) due to the high carrier activation rate of H^- at O^{2-} site,²⁴ which limits ZT enhancement to the low x region. Further improvement of ZT requires increasing anion-site defects to reduce κ_{lat} , while simultaneously controlling the carrier concentration to remain within the optimal range. Excessive anion-site defects lead to too high carrier densities, which deteriorate the PF due to reduced Seebeck coefficient.

In addition, the $\text{SrTiO}_{3-x}\text{H}_x$ bulk polycrystals require the complex and time-consuming synthesis processes: first, the $\text{SrTiO}_{3-x}\text{H}_x$ powders were prepared through low- T topochemical reaction between parent SrTiO_3 precursors and calcium hydride (CaH_2),^{28,29} and then densified into bulk polycrystals by spark plasma sintering (SPS). The topochemical reaction of SrTiO_3 with CaH_2 needs heat treatment for a long time (~ 7 days). Moreover, the washing process for the obtained $\text{SrTiO}_{3-x}\text{H}_x$ powders is necessary to remove the residual CaH_2 and byproduct CaO . Such complex and time-consuming process is unsuitable for future thermoelectric applications. In addition, since the CaH_2 is a strong reductant, the topochemical reaction of $\text{SrTiO}_{3-x}\text{H}_x$ at $T \geq 500$ °C results in the decomposition, observed by increasing amounts of TiH_2 impurity. On the other hand, after the high- T sintering by SPS, the oxidized TiO_x impurities are formed in bulk polycrystal, and their volume fractions increase up to 12 mol% for $\text{SrTiO}_{3-x}\text{H}_x$ bulks.²⁴ Moreover, due to the loss of H during high- T SPS process, oxygen vacancies (V_{O}) should be formed in the $\text{SrTiO}_{3-x}\text{H}_x$ bulks, and the V_{O} formation provide strong phonon scattering. However, the presence of impurities made it difficult to quantify both H^- and V_{O} concentrations, hindering an understanding of their respective contributions to the κ_{lat} reduction in the $\text{SrTiO}_{3-x}\text{H}_x$. The

preparation of high phase-purity $\text{SrTiO}_{3-x}\text{H}_x$ powders and bulk polycrystals with controlled x and the amounts of V_{O} is still a challenge to clarify the effect of the H substitution and V_{O} formation on electronic and thermoelectric properties.

In this paper, we demonstrate the synthesis of high phase-purity, heavily H-doped $\text{SrTiO}_{3-x}\text{H}_x$ powders by the solid-state reaction of SrO , SrH_2 , and TiO_2 as the starting materials. We previously reported the direct synthesis of heavily H-doped hexagonal $\text{BaTiO}_{3-x}\text{H}_x$ ($x \sim 1$) powders through the solid-state reaction of BaH_2 with TiO_2 at a relatively low $T = 800$ °C under H_2 gas flow.³⁰ $\text{SrTiO}_{3-x}\text{H}_x$ powders were synthesized in a similar manner to hexagonal $\text{BaTiO}_{3-x}\text{H}_x$, but the samples contained many impurity phases. In this work, we applied solid-state reaction at much higher $T > 1000$ °C in a H_2 -filled silica-glass tube. The amount of impurity phase was largely decreased at higher T , and single phase $\text{SrTiO}_{3-x}\text{H}_x$ powders with $x = 0.17\text{--}0.37$ were obtained at $T = 1100$ °C. On the other hand, subsequent SPS sintering yielded highly dense $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\text{O}\delta}$ bulk polycrystals containing large amounts of both H and V_{O} , where the total concentration of $x + \delta$ was controlled over a wide range from 0.13 to 0.40. The carrier activation rate of H^- was nearly 100%, while that of V_{O} was only 23–27% in $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\text{O}\delta}$ bulks, enabling the low κ_{lat} and high PF even at high $x + \delta$ values. We investigated the electronic and phonon transport properties of $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\text{O}\delta}$ bulks, and discussed the effects of H^- and V_{O} on phonon scattering with assistance of first-principles calculations.

2. EXPERIMENTAL SECTION

2.1. Bulk synthesis. $\text{SrTiO}_{3-x}\text{H}_x$ powders were synthesized by high- T solid-state reactions of $(1-x)\text{SrO} + x\text{SrH}_2 + \text{TiO}_2 \rightarrow \text{SrTiO}_{3-x}\text{H}_x + 0.5x\text{H}_2$. First, fresh Sr metal (99.9%, Aldrich) was

finely cut into small pieces of grains,³¹ and the Sr grain was annealed in H₂ gas at 400 °C for 20 h to prepare SrH₂ powder. The SrO powder was obtained by decarbonization of SrCO₃ powder (99.5%, Kojundo kagaku) at 1200 °C in air. Then the powders of SrH₂, SrO, and TiO₂ (99.999%, Kojundo Kagaku) were mixed and pressed into pellets in 10-mm diameter. The handling of starting materials was performed in a glovebox with a dry inert Ar gas (the dew point <−100 °C, the oxygen concentration < 1 ppm). The obtained pellet was wrapped in Mo foil and then sealed with H₂-filled silica-glass tube (the inside of the silica-glass ampule was vacuumed, and then, H₂ gas was filled at ~1 atm at RT before sealing the glass tube). The sealed tube was heated at 1000–1100 °C for 20 h. The obtained SrTiO_{3-x}H_x powders were reground and pressed into 10-mm ϕ pellets. The SrTiO_{3-x}H_x pellet was sealed with a stainless capsule. The sealed pellet was densified rapidly by SPS under 80 MPa at $T = 1150$ °C in vacuum, resulting in the SrTiO_{3-x- δ} H_xV_{O δ} bulks. After that, the stuck Mo foil and stainless capsule were peeled off, and the sample surface was polished. For comparison, a SrTiO₃ polycrystal was prepared by the SPS in vacuum, where the SrTiO₃ bulk was annealed in air to reduce V_O fomed during the SPS process.

2.2. Crystal structure and chemical composition analysis. Crystalline phases for SrTiO_{3-x}H_x powders and SrTiO_{3-x- δ} H_xV_{O δ} bulks were examined by X-ray diffraction (XRD) with the Bragg–Brentano geometry with a Cu K α radiation source. The lattice parameters were determined by the Pawley method using the TOPAS ver. 4.2 program (Karlsruhe, Germany: Bruker AXS GmbH). Time-of-flight neutron powder diffraction (NPD) measurements were carried out using a NOVA neutron total scattering instrument (BL21 beamline) at the Japan Proton Accelerator Research Complex (J-PARC). The measurement was performed for fine powders by crushing the sintered SrTiO_{3-x- δ} H_xV_{O δ} bulks. The white neutron beam intensity at J-PARC was 800 kW. The

crystal structures were analyzed by Rietveld refinement using the computer program Z-Rietveld (Ver. 1.1.3).^{32,33}

Microstructures and chemical composition mappings of the $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\text{O}\delta}$ bulks were observed by electron probe microanalyzer (EPMA). The H concentration (x) was measured by the thermal desorption spectroscopy (TDS), and the V_{O} concentration (δ) was estimated by thermogravimetric analysis (TGA) for $\text{SrTiO}_{3-x}\text{H}_x$ powders and $\text{SrTiO}_{3-x-y}\text{H}_x\text{V}_{\text{O}y}$ bulks. The measurements for $\text{SrTiO}_{3-x-y}\text{H}_x\text{V}_{\text{O}y}$ were performed by crushing the sintered bulks to fine powders. TDS measurement was performed under ultra-high vacuum condition, in order to detect the H release from the samples at high T . TGA measurement was performed in air to oxidize the samples, where they exhibited a weight gain with increasing temperature due to the replacement of H and V_{O} with oxygen from the atmosphere. Therefore, the total concentration of H and V_{O} can be estimated from TGA data.

2.3. Electronic and thermal transport properties. Electronic and thermal transport properties were characterized for the $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\text{O}\delta}$ bulks. σ and S were simultaneously measured by four-probe method with a ZEM-3 (ADVANCE-RIKO, Inc.) under a Helium atmosphere. The κ was obtained from $\kappa = D \cdot C \cdot d$, where the thermal diffusivity (D) along out-of-plane direction in the bulk was measured in an Argon atmosphere by a laser flash diffusivity method (LFA 457, NETZSCH) and the heat capacity (C) was measured by differential scanning calorimetry (DSCvesta, Rigaku Corp.), and the sample density (d) was determined by the dimensions and mass of the samples. Low- T Hall effect was measured under applied magnetic field up to ± 5 T with a physical property measurement system (PPMS, Quantum Design). The carrier concentration was calculated by $n = 1/e|R_{\text{H}}|$ and Hall mobility was calculated by $\mu = \sigma/(en)$, where R_{H} is Hall coefficient and e is the elementary charge.

2.4. Phonon transport calculations. Density functional theory (DFT) calculations were conducted using the projector augmented wave (PAW) method as implemented in the Vienna Ab initio Simulation Package (VASP) code^{34,35} with the generalized gradient approximation (GGA) Perdew–Burke–Ernzerhof (PBE) functional.³⁶ Crystal structures were optimized with a plane wave cutoff energy of 600 eV. A $2 \times 2 \times 2$ supercell of the fully-relaxed SrTiO_3 primitive cell was constructed containing 8 Sr atoms, 8 Ti atoms, and 24 O atoms. Then, two O atoms were substituted with H atoms to create $\text{SrTiO}_{2.75}\text{H}_{0.25}$ model. Subsequently, these H atoms were removed from the substituted O sites to create the oxygen-deficient $\text{SrTiO}_{2.75}\text{V}_{0.25}$ model. Phonon transport properties for SrTiO_3 , $\text{SrTiO}_{2.75}\text{H}_{0.25}$, and $\text{SrTiO}_{2.75}\text{V}_{0.25}$ were calculated using the ALAMODE code,^{37,38} with detailed settings referring to our previous work.²⁴

3. RESULTS AND DISCUSSION

3.1. Synthesis. First, we optimized the annealing temperatures (T_A) from 1000 °C to 1100 °C for the synthesis of high-purity $\text{SrTiO}_{3-x}\text{H}_x$ powders with a nominal $x = 0.2$ (**Figure 1a**). At $T_A = 1000$ °C, the diffraction peaks corresponding to the cubic SrTiO_3 phase (space group: $Pm\bar{3}m$) was observed, as indicated by the vertical black lines. On the other hand, several diffraction peaks that could not be assigned to the cubic SrTiO_3 phase were observed and were identified as impurity phases, including Sr_2TiO_4 , $\text{Sr}_3\text{Ti}_2\text{O}_7$, $\text{Sr}(\text{OH})_2$, Ti_2O_3 . With increase of T_A , the formation of the impurity phases was suppressed at $T_A = 1050$ °C, and then single phase $\text{SrTiO}_{3-x}\text{H}_x$ powder was obtained at $T_A = 1100$ °C. **Figure 1b** summarizes the XRD patterns at RT for $\text{SrTiO}_{3-x}\text{H}_x$ powders with nominal $x = 0.2$ – 0.4 , synthesized at the optimized $T_A = 1100$ °C. For comparison, the XRD pattern of pure SrTiO_3 powder is also shown. All diffraction peaks are assigned to the cubic SrTiO_3

phase without any impurity phases. The cubic lattice parameters (a), refined by Rietveld analysis of XRD patterns, increases proportionally from 3.905 Å for pure SrTiO₃ to 3.911 Å for SrTiO_{3-x}H_x with nominal $x = 0.4$ (**Figure 1c**). Consequently, the lattice volume (V) expands from 59.547 to 59.836 Å³. The lattice expansion is attributed to the larger ion radius of H⁻ (1.54 Å) compared to O²⁻ (1.38 Å),²⁹ as well as the larger ion radius of Ti³⁺ (0.67 Å) than compared to Ti⁴⁺ (0.61 Å).^{39,40} In addition to these ion size differences, the lattice expansion may also result from the longer and weaker Ti-H and Sr-H bonds than Ti-O and Sr-O bonds in the Ti-(O,H)₆ octahedra and Sr-(O,H)₁₂ polyhedra (See ref 24). **Figure 1d** shows the relationship between the nominal x and the measured x for H concentration, as well as δ for V_O concentration in SrTiO_{3-x-δ}H_xV_{Oδ}. The TDS and TGA spectra are summarized in **Figure S1** of Supporting Information. The measured x increased from 0.17 to 0.37, and there is a good agreement between the nominal and measured x values, indicating that H was incorporated almost exactly as designed. Additionally, the V_O concentration (δ) is less than 0.005 for all samples and remains nearly unchanged across the range of nominal x . Therefore, the high-purity SrTiO_{3-x}H_x powders with measured $x = 0.17$ to 0.37 were successfully synthesized via the high- T solid-state reaction without significant H loss, i.e., V_O formation.

Next, we performed SPS for the single-phase SrTiO_{3-x}H_x powders to obtain dense SrTiO_{3-x-δ}H_xV_{Oδ} bulks at a sintering temperature of 1050 °C. For all nominal x compositions, single-phase, high-purity bulk samples were obtained without the formation of any impurity phases (**Figure 2a**), and the a increases monotonically with nominal x (**Figure 2b**), similarly observed in SrTiO_{3-x}H_x powders. The TDS and TGA spectra for SrTiO_{3-x-δ}H_xV_{Oδ} bulks are summarized in **Figure S2** of Supporting Information. The measured x values for the bulk samples

increased from 0.06 to 0.27 but became smaller than the corresponding nominal x values (**Figure 2c**). Meanwhile, the V_O concentration (δ) increased with increase of nominal x , yielding the compositions of $\text{SrTiO}_{2.87}\text{H}_{0.06}\text{V}_{0.07}$ for the nominal $x = 0.2$ sample, $\text{SrTiO}_{2.73}\text{H}_{0.16}\text{V}_{0.11}$ for $x = 0.3$, and $\text{SrTiO}_{2.60}\text{H}_{0.27}\text{V}_{0.13}$ for $x = 0.4$, respectively. The sintered $\text{SrTiO}_{3-x}\text{H}_x$ bulks contained both H and V_O , with x controlled in the range of 0.06 to 0.27 and δ in the range of 0.07 to 0.13. The sum of the measured x and δ values closely matched the nominal x values, suggesting the formation of V_O during the high- T SPS process. The sintered density for all samples was $\sim 93\%$, and the average grain sizes ranged from 200 to 500 nm (**Figure S3** of Supporting Information). We performed NPD measurements for the $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\delta}$ bulk samples to estimate the amount of H and V_O at O sites. For comparison, the NPD measurement was also performed for SrTiO_3 bulk. The NPD patterns and Rietveld analyses are summarized in **Figure S4** and **Tables S1, S2** of Supporting Information. The chemical composition for pure SrTiO_3 bulk was estimated to be $\text{SrTi}_{0.99}\text{O}_{3.00}$ with negligible formation of V_O . On the other hand, the chemical compositions for $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\delta}$ bulks were estimated to be $\text{Sr}_{0.99}\text{Ti}_{0.99}\text{O}_{2.88}\text{H}_{0.09}\text{V}_{0.03}$ for the nominal $x = 0.2$ sample and $\text{SrTi}_{0.97}\text{O}_{2.72}\text{H}_{0.23}\text{V}_{0.05}$ for $x = 0.4$. It should be noted that the H substitution and V_O formation at O site induce the local structure distortion in Ti-O_6 octahedra, resulting in distributions in the bond length of Ti-O and the bond angles of O-Ti-O and Ti-O-Ti, as discussed later. Although the local structure is expected to exhibit lower symmetry, the NPD data were analyzed assuming a high-symmetric cubic structure that represents the averaged global structures. As a result of the refinement, it was found that the atomic displacement parameters (**Table S1**) obtained from Rietveld refinement for $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\delta}$ are larger than that of the pure SrTiO_3 with the ideal cubic structure, presumably

reflecting the spatial distribution of local distortions in the Ti–O₆ octahedra. Although the absolute values of measured x and δ obtained from TDS and TGA spectra differ slightly from the NPD results, their increasing trends with respect to nominal x are almost consistent. The incorporated H is predominantly substituted at the O site. It is known that V_O can be formed in SrTiO₃ by heating in highly reducing condition (H₂ gas) at high T . The reported V_O concentration (δ) is only 0.06 in SrTiO_{3- δ} polycrystal.⁴¹ It can be considered that by using SrTiO_{3- x} H _{x} powder samples with high x , bulk samples containing not only a large amount of H but also significant numbers of V_O can be fabricated, which should be expected to provide strong phonon scattering and reduce κ_{lat} .

3.2. Thermal transport properties. Figure 3a show the T dependence of total κ and electronic κ (κ_{ele}) of SrTiO_{3- x} H _{x} $V_{O\delta}$ bulks. The T dependences of heat capacity and thermal diffusivity are summarized in Figure S5 of Supporting Information. The κ_{ele} was calculated by Wiedemann-Franz law as $\kappa_{\text{ele}} = LT\sigma$, where the Lorenz number L is calculated by the single parabolic band model using the Fermi level estimated from the measured S .⁴² The σ and S will be shown later. The κ of all SrTiO_{3- x} H _{x} $V_{O\delta}$ bulks showed monotonic decrease with the increase of T . The κ at $T = 300$ K decreased from 6.45 W/(mK) to 5.26 W/(mK) with the increase of x from 0.06 to 0.27 and δ from 0.07 to 0.13. The κ_{ele} at $T = 300$ K increased from 0.67 W/(mK) to 1.49 W/(mK) due to the increase of σ by the increase of H⁻ and V_O donors, as will be discussed later. Then, the lattice κ (κ_{lat}) was calculated by subtracting the electronic contribution from the total κ , i.e., $\kappa_{\text{lat}} = \kappa - \kappa_{\text{ele}}$ (Figure 3b). The κ_{lat} of pure SrTiO₃ bulk and reported κ_{lat} of SrTiO_{2.94} $V_{O0.06}$ bulk⁴¹ are also shown to discuss the effect of H⁻ substitution and V_O formation on κ_{lat} of the present SrTiO_{3- x} H _{x} $V_{O\delta}$

bulks. The κ_{lat} at $T = 300$ K largely decreased from 8.22 W/(mK) of pure SrTiO_3 bulk to 5.78 W/(mK) for $\text{SrTiO}_{2.87}\text{H}_{0.06}\text{V}_{0.07}$ bulk, and κ_{lat} was further reduced to 4.17 W/(mK) for $\text{SrTiO}_{2.73}\text{H}_{0.16}\text{V}_{0.11}$ bulk, which is 49% lower than that of pure SrTiO_3 . The κ_{lat} at high $T = 673$ K was also reduced from 4.58 W/(mK) of SrTiO_3 bulk to 3.46 W/(mK) of $\text{SrTiO}_{2.73}\text{H}_{0.16}\text{V}_{0.11}$ bulk, indicating that the H substitution and V_O formation enhanced the phonon scattering in the wide T range. On the other hand, even if the x and δ was further increased, the κ_{lat} reduction was saturated at 4.02 W/(mK) for $\text{SrTiO}_{2.60}\text{H}_{0.27}\text{V}_{0.13}$ bulk and the κ_{lat} showed an almost negligible T dependence. This result suggests that phonon scattering induced by H^- substitution and V_O formation reaches an upper limit. As shown in **Fig. 4(e)**, since O vibrations primarily contribute to high-frequency optical phonon modes, the phonon scattering induced by H^- substitution and V_O formation predominantly affects the high-frequency phonons. However, thermal transport in SrTiO_3 is also governed by low-frequency phonons mainly from Sr atomic vibrations. Therefore, further reduction in κ_{lat} would require scattering mechanisms for low-frequency phonons for example, through defect engineering at the Sr site.¹⁹⁻²² Compared to the κ_{lat} of 6.5 W/(mK) at $T = 322$ K for the reported $\text{SrTiO}_{2.94}\text{V}_{0.06}$ bulk, the κ_{lat} was significantly reduced due to the large amount of H^- and V_O in present $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\text{O}\delta}$ bulks. As discussed later, H^- substitution and V_O formation introduce local structure distortions in the Ti-O_6 octahedra, which result in strong phonon scattering. As the concentrations of H^- and V_O increase, the phonon scattering becomes stronger, leading to a significant reduction in κ_{lat} .

3.3. Phonon transport calculations. To understand the effect of the H substitution and V_O formation on the reduction of κ_{lat} , we performed anharmonic phonon calculations using SrTiO_3 , $\text{SrTiO}_{2.75}\text{V}_{0.25}$, and $\text{SrTiO}_{2.75}\text{H}_{0.25}$ models. To create the $\text{SrTiO}_{2.75}\text{H}_{0.25}$ model, two O atoms of

cubic SrTiO_3 model were replaced with H atoms. Owing to the crystalline symmetry, seven different configurations are possible for placing the two H atoms at O sites. See Ref. 24 for the detailed H positions in the $\text{SrTiO}_{2.75}\text{H}_{0.25}$ models. The difference in total energy of the $\text{SrTiO}_{2.75}\text{H}_{0.25}$ models with different H positions is as small as 14 meV/atom, indicating that all models can coexist in the experimental samples synthesized at finite temperatures, which is consistent with the random distribution of O and H at the anion sites (**Table S1**). To simplify, among them, we used the H configuration yielding the lowest κ_{lat} in $\text{SrTiO}_{2.75}\text{H}_{0.25}$ model, where the two H atoms are substituted at O site on the Sr–O plane in diagonally opposite (cater-cornered) Ti–O₆ octahedra (**Figure S6a** of Supporting Information). By removing the two H atoms from the substituted O sites, we constructed the $\text{SrTiO}_{2.75}\text{V}_{0.25}$ model. **Figures 4a–c** compare the phonon dispersion and partial phonon density of states (DOSs) of cubic SrTiO_3 , $\text{SrTiO}_{2.75}\text{V}_{0.25}$, and $\text{SrTiO}_{2.75}\text{H}_{0.25}$ models. The corresponding harmonic phonon dispersions are provided in **Figure S7** of Supporting Information. For cubic SrTiO_3 , the optical phonon bands, dominated by Ti and O atomic vibrations, are highly dispersive at high frequencies of 4–15 THz (**Figure 4a**). The dispersion is much larger than the low-frequency acoustic phonon bands (< 4 THz), arising from Sr atomic vibrations. In contrast, $\text{SrTiO}_{2.75}\text{H}_{0.25}$ and $\text{SrTiO}_{2.75}\text{V}_{0.25}$ models similarly exhibit nondegenerate phonon bands than cubic SrTiO_3 (**Figures 4b,c**), due to the local structure distortion with distributions in the bond length of Ti–O and the bond angles of O–Ti–O and Ti–O–Ti caused by the H substitution and V_O formation (**Figure S6b** of Supporting Information), resulting in the splitting of degenerated phonon bands. Particularly, the optical phonon bands become flatter due to fluctuations in the Ti–(O,H) bonding environment, and the slopes of the acoustic phonon branches decrease along the Γ –X and Γ –M directions. Notably, the substituted H in $\text{SrTiO}_{2.75}\text{H}_{0.25}$ introduces localized phonon modes at high frequencies of ~24 THz and ~37 THz (**Figure 4b**),

but due to their low group velocity and isolation from lower-frequency modes, they contribute negligibly to phonon transport and anharmonic phonon scattering in $\text{SrTiO}_{2.75}\text{H}_{0.25}$. Note that cubic SrTiO_3 shows a low-frequency soft-phonon mode at R point (**Figure 4a**), which primarily originates from the antiferrodistortive (AFD) rotation of Ti-O_6 octahedra and is closely related to the instability of the cubic structure.⁴³ A similar low-frequency phonon mode appears at Γ point (corresponding to the symmetry-transferred R point) in both $\text{SrTiO}_{2.75}\text{H}_{0.25}$ and $\text{SrTiO}_{2.75}\text{V}_{0.25}$ models (**Figures S7b,c**).

Figure 4d compares the T dependence of calculated κ_{lat} for SrTiO_3 , $\text{SrTiO}_{2.75}\text{V}_{0.25}$, and $\text{SrTiO}_{2.75}\text{H}_{0.25}$ models. The calculated κ_{lat} at $T = 300$ K largely decreases from 9.18 W/(mK) for SrTiO_3 to 2.85 W/(mK) for $\text{SrTiO}_{2.75}\text{H}_{0.25}$ and 2.24 W/(mK) for $\text{SrTiO}_{2.75}\text{V}_{0.25}$. Note that the calculated κ_{lat} for $\text{SrTiO}_{2.75}\text{H}_{0.25}$ and $\text{SrTiO}_{2.75}\text{V}_{0.25}$ is lower than the experimental values, likely due to the dependence of κ_{lat} on the H substitution and V_O formation sites.²⁴ **Figure 4e** shows the κ_{lat} spectra at $T = 300$ K as a function of the phonon frequency. In SrTiO_3 , the major contribution to the total κ_{lat} arises from phonons with frequencies below 15 THz. Both the H substitution and V_O formation significantly reduce κ_{lat} by suppressing the contribution from the low-frequency phonons. **Figure 4f** shows the cumulative κ_{lat} with respect to the phonon mean free path (l_{ph}). The κ_{lat} of SrTiO_3 is dominated by phonons with the l_{ph} shorter than 10 nm, while their phonon transport is significantly suppressed by the H substitution and V_O formation. **Figures 4g-i** compare the l_{ph} , the phonon group velocity (v_{ph}), and the phonon lifetime (τ_{ph}) in terms of the phonon frequency. For SrTiO_3 , the τ_{ph} is small at frequencies > 4 THz (**Figure 4i**), but the v_{ph} is large in wide phonon frequency range (**Figure 4h**), reflecting the widely spread optical phonon bands. The H substitution and V_O formation reduce both the τ_{ph} and v_{ph} of SrTiO_3 , resulting in the shorter l_{ph}

in the wide frequency range (**Figure 4g**). The reduction of ν_{ph} originates from the flatter optical phonon bands and the downward shift of acoustic phonon branches associated with Sr atomic vibrations around ~ 3 THz, suggesting the enhanced Umklapp scattering due to the acoustic and optical phonon interaction (**Figures 4b,c**). These results indicate that the H substitution and V_{O} formation have comparable effects on phonon transport properties. The underlying origin of the similar behaviors of H^- substitution and V_{O} formation is further discussed in the following section.

We previously reported that the reduction in κ_{lat} for $\text{SrTiO}_{2.75}\text{H}_{0.25}$ originates from local structure distortion, specifically the heterogeneity of Ti–(O,H) bond lengths induced by the H substitution.²⁴ The relationship between the calculated κ_{lat} and the distortion of Ti–(O,H) bond lengths for the SrTiO_3 , $\text{SrTiO}_{2.75}\text{V}_{0.25}$, and $\text{SrTiO}_{2.75}\text{H}_{0.25}$ models is shown in **Figure S8** of Supporting Information. Both the H substitution and V_{O} formation cause similar distortions in the Ti–O₆ octahedra, resulting in the comparable κ_{lat} values. The H substitution and V_{O} formation break the local structural symmetry and induce additional modulation of the force constants, leading to splitting of degenerate phonon modes and the observed reduction in phonon dispersion. These broad frequency shifts enhance the phonon-phonon scattering, which results in large τ_{ph} reduction in SrTiO_3 . We analyzed the chemical bonding characteristics of the Ti–O and Ti–H bonds in $\text{SrTiO}_{2.75}\text{H}_{0.25}$ model using the crystal orbital Hamiltonian overlap (COHP),⁴⁴ calculated by the LOBSTER codes.⁴⁵ The –COHP for the Ti–O and Ti–H bonds is shown in **Figure S9** of Supporting Information. The averaged –iCOHP value of the Ti–O bonds is 3.58 eV/bond, indicating a strong covalent interaction between the Ti and O atoms, while that of the Ti–H bond is only 0.96 eV/bond, suggesting a more ionic nature of the Ti and H atom interaction. Due to the

significantly weaker Ti–H bonds, H behaves similarly to V_O in the Ti–O₆ octahedra, as V_O effectively removes a Ti–O bond entirely.

3.4. Thermoelectric properties. σ and S for the $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{O\delta}$ bulks as a function of T are summarized in **Figures 5a,b**. We confirmed that the σ and S for all $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{O\delta}$ bulks were reversibly reproduced during heating and cooling cycles in the T range between 300 K (RT) and 673 K (400 °C), indicating that H does not desorb from bulks at this T range. All $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{O\delta}$ bulks exhibited metallic T dependence of σ (**Figure 5a**). The σ at $T = 300$ K increased from 1260 S/cm to 2350 S/cm with the increase of H and V_O concentrations ($x + \delta$) from 0.13 to 0.27, but it decreased to 1850 S/cm for higher $x + \delta$ values of 0.40. All the samples showed negative S in the whole T range (**Figure 5b**), indicating the majority carrier is electron, consistent with the fact that H^- and V_O act as donor. The absolute values of S ($|S|$) at $T = 300$ K monotonically decreased from 129 $\mu\text{V/K}$ to 47 $\mu\text{V/K}$ with the increase of $x + \delta$ from 0.13 to 0.40, and the $|S|$ values for all samples increased with increasing T . **Figures 5c,d** show the low- T carrier mobility (μ) and carrier concentration (n). The n for all samples exhibited almost no T dependence, indicating degenerated electron conduction. The n at $T = 300$ K increased from $1.7 \times 10^{21} \text{ cm}^{-3}$ for $x + \delta = 0.13$ to $5.8 \times 10^{21} \text{ cm}^{-3}$ for $x + \delta = 0.40$ (**Figure 5d**). The dotted lines indicate the $n_{\text{H}+\text{VO}}$, estimated by considering that all H^- at O^{2-} site provides one electron and V_O gives two electrons in the $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{O\delta}$. The $n_{\text{H}+\text{VO}}$ is larger than measured n for all samples regardless of $x + \delta$. It is reported that the carrier activation rate of H^- in $\text{SrTiO}_{3-x}\text{H}_x$ thin films is almost 100%,⁴⁶ while the carrier activation rate of V_O in $\text{SrTiO}_{3-\delta}$ single crystal is as low as 25–53%.⁴⁷ By considering the 100% activation rate of H^- , we estimated the carrier activation rate of V_O to be 23–27% in $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{O\delta}$ bulks. The μ

at $T = 300$ K decreased from $4.6 \text{ cm}^2/(\text{Vs})$ for $x + \delta = 0.13$ to $1.9 \text{ cm}^2/(\text{Vs})$ for $x + \delta = 0.40$, but all samples exhibited a trend of increasing μ at lower T . Detailed μ analyses at low $T \leq 300$ K as well as high $T \geq 300$ K are summarized in **Figure S10** of Supporting Information. The μ of the $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\text{O}\delta}$ bulks is limited mainly by impurity scattering and electron-electron scattering at low T and that is limited by optical phonon scattering at high T . The higher concentration of H and V_{O} results in the increase of impurity scattering and electron-electron scattering due to increase of n . On the other hand, grain boundary scattering is negligible across the entire T range in $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\text{O}\delta}$ bulks even with its polycrystalline form.

Figures 5e,f summarize PF ($= S^2\sigma$) and ZT of the $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\text{O}\delta}$ bulks. PF at $T = 300$ K decreased from 20.9 to $4.1 \text{ }\mu\text{W}/(\text{cmK}^2)$ with the increase of $x + \delta$ from 0.13 to 0.40 due to the decrease of S (**Figure 5e**). However, for $\text{SrTiO}_{2.73}\text{H}_{0.16}\text{V}_{\text{O}0.11}$ and $\text{SrTiO}_{2.60}\text{H}_{0.27}\text{V}_{\text{O}0.13}$ bulks, the PF increased to 8.1 and $12.8 \text{ }\mu\text{W}/(\text{cmK}^2)$ with increasing T up to 648 K, respectively. On the other hand, the PF for $\text{SrTiO}_{2.87}\text{H}_{0.06}\text{V}_{\text{O}0.07}$ decreased to $12.0 \text{ }\mu\text{W}/(\text{cmK}^2)$ at $T = 673$ K. The $\text{SrTiO}_{2.87}\text{H}_{0.06}\text{V}_{\text{O}0.07}$ bulk with $x + \delta = 0.13$ exhibited the highest $ZT = \sim 0.1$ at $T = 300$ K (**Figure 5f**) and ZT value increased continuously up to 0.18 at $T = 673$ K. On the other hand, $\text{SrTiO}_{2.73}\text{H}_{0.16}\text{V}_{\text{O}0.11}$ bulk with $x + \delta = 0.27$ showed the highest $ZT = 0.21$ at $T = 673$ K. Owing to the significant reduction in the κ_{lat} , the ZT of $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\text{O}\delta}$ bulk at $T = 300$ K is more than 5-times higher than 0.01 – 0.02 reported for La-doped SrTiO_3 polycrystals,⁴⁸ and exceeds the ZT values of 0.07 – 0.08 for the La-doped SrTiO_3 single crystals.^{13,15,49}

4. CONCLUSIONS

We reported the synthesis and thermoelectric properties of $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\text{O}\delta}$ bulk polycrystals with complex anion-site defects, containing large amounts of both H and V_{O} , with the total concentration of $x + \delta$ controlled over a wide range from 0.13 to 0.40. The $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\text{O}\delta}$ bulks were prepared by a high- T solid-state reaction ($\text{SrH}_2 + \text{SrO} + \text{TiO}_2 \rightarrow \text{SrTiO}_{3-x}\text{H}_x$ with $x = 0.17\text{--}0.37$), followed by high- T SPS, during which partial H loss occurred. This process enables large-scale synthesis in a shorter time and simpler process compared to conventional topochemical reaction methods. As increasing $x + \delta$ values, κ_{lat} at $T = 300$ K largely decreased from 8.22 W/(mK) for pure SrTiO_3 to 4.02 W/(mK) for $\text{SrTiO}_{2.60}\text{H}_{0.27}\text{V}_{\text{O}0.13}$. It was found that both H and V_{O} contribute almost equally to phonon scattering, attributed to local structure distortions in Ti-O_6 octahedra. On the other hand, while the carrier activation rate of H^- was nearly 100%, that of V_{O} was only 23–27% in $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\text{O}\delta}$ bulks. This enabled decoupled control of electronic and phonon transport, achieving both low κ_{lat} and high PF even at high $x + \delta$ values. The highest ZT value of ~ 0.1 was obtained at $T = 300$ K for $\text{SrTiO}_{2.87}\text{H}_{0.06}\text{V}_{\text{O}0.07}$, while it increased to 0.21 at $T = 673$ K for $\text{SrTiO}_{2.73}\text{H}_{0.16}\text{V}_{\text{O}0.11}$. These results highlight that anion-site defect engineering via mixed anion substitution and vacancy formation is a promising strategy for further reducing κ_{lat} and enhancing the performance of thermoelectric oxides. For example, incorporating H, V_{O} , and other anions such as nitrogen, which acts as an acceptor,⁵⁰ is expected to achieve even lower κ_{lat} and higher ZT . In addition, the combination of cation-site and anion-site defects could offer an even more powerful strategy. Note that direct mechanochemical reactions have been reported for synthesizing fine powders of hydride-substituted perovskite oxides without the need of

heat treatment.⁵¹ The combination of mechanochemical synthesis and subsequent sintering represents a promising approach with a simpler and more scalable process.

ASSOCIATE CONTENT

Supporting Information

Supporting Information is available free of charge.

Crystal structure, microstructure, and chemical composition analyses of $\text{SrTiO}_{3-x}\text{H}_x$ powders and $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{0\delta}$ bulks. Temperature dependence of heat capacity and thermal diffusivity, as well as carrier mobility analyses of $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{0\delta}$ bulks. Phonon transport, crystal structure, and chemical bonding analyses of SrTiO_3 , $\text{SrTiO}_{2.75}\text{H}_{0.25}$, and $\text{SrTiO}_{2.75}\text{V}_{00.25}$ models by DFT calculations.

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Note

The authors declare no conflict of interest.

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Figures

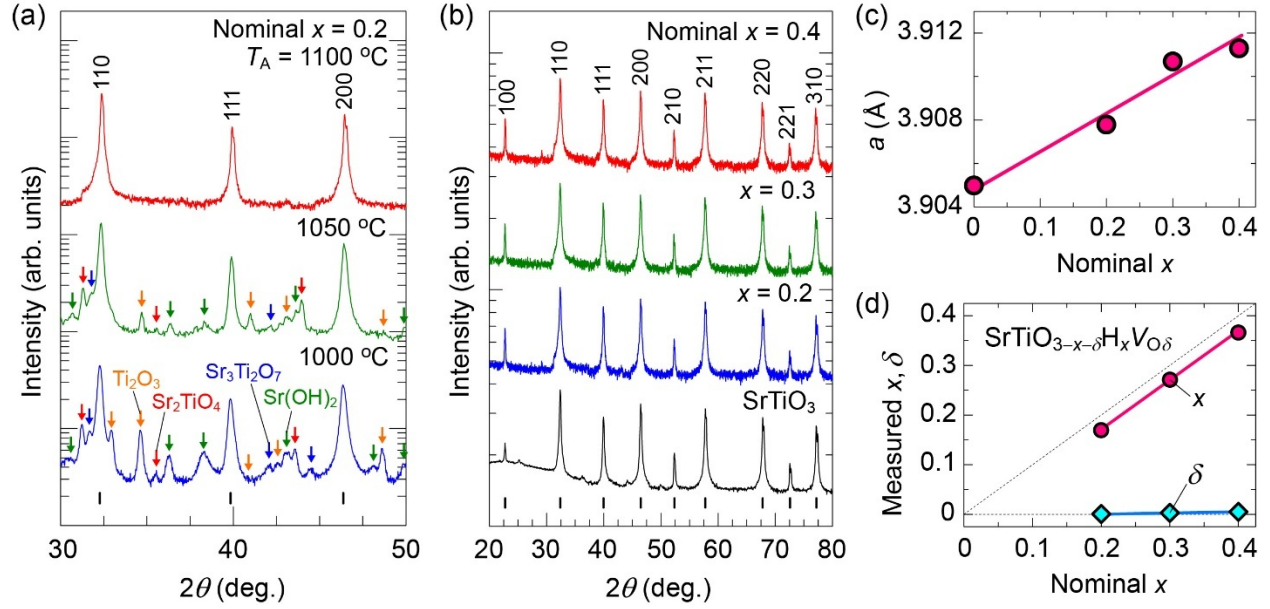


Figure 1. (a) XRD patterns of $\text{SrTiO}_{3-x}\text{H}_x$ powders with a nominal $x = 0.2$ synthesized by solid-state reaction at various temperatures of $T_A = 1000\text{--}1100$ °C. Black vertical bars indicate the diffraction peak positions for cubic perovskite SrTiO_3 phase (space group $Pm\bar{3}m$). Red, blue, green, and orange arrows denote the diffraction peaks from impurity phases of Sr_2TiO_4 , $\text{Sr}_3\text{Ti}_2\text{O}_7$, $\text{Sr}(\text{OH})_2$, and Ti_2O_3 , respectively. (b) Wide-range XRD patterns for $\text{SrTiO}_{3-x}\text{H}_x$ powders with nominal $x = 0.2\text{--}0.4$. (c) Lattice parameter (a) as a function of nominal x for $\text{SrTiO}_{3-x}\text{H}_x$ powders. For comparison, XRD pattern and lattice parameter of pure SrTiO_3 powder are also shown in (b,c). (d) Relationship between the nominal x and the measured x for H concentration, as well as δ for V_O concentration in $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{O\delta}$.

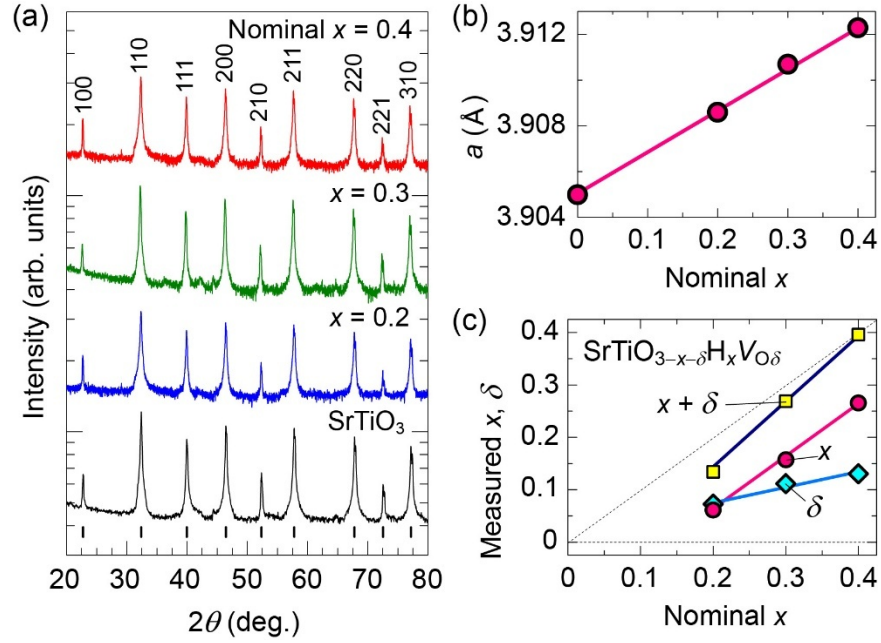


Figure 2. (a) XRD patterns of $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{VO}_\delta$ bulks obtained by sintering $\text{SrTiO}_{3-x}\text{H}_x$ powders with nominal $x = 0.2\text{--}0.4$. The black vertical bars denote the diffraction angles of the cubic perovskite structure (space group: $Pm\bar{3}m$). (b) Lattice parameter (a) as a function of nominal x . For comparison, XRD pattern and lattice parameter of SrTiO_3 bulk are also shown in (a,b). (c) Measured x and δ in $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{VO}_\delta$ bulks as a function of nominal x . The yellow plots are the sum of x and δ .

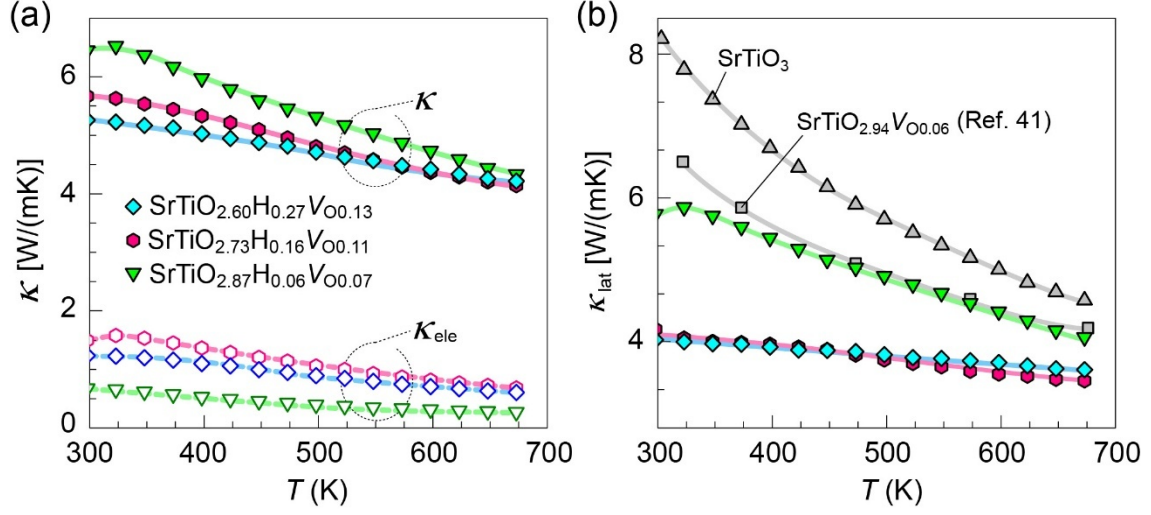


Figure 3. T dependences of (a) total thermal conductivity (κ) and electronic κ (κ_{ele}), (b) lattice κ (κ_{lat}) for $\text{SrTiO}_{3-x}\text{H}_x\text{VO}_\delta$ bulks. The κ_{lat} of pure SrTiO_3 bulk and the reported κ_{lat} of $\text{SrTiO}_{2.94}\text{VO}_{0.06}$ bulk³⁷ are shown in (b) for comparison.

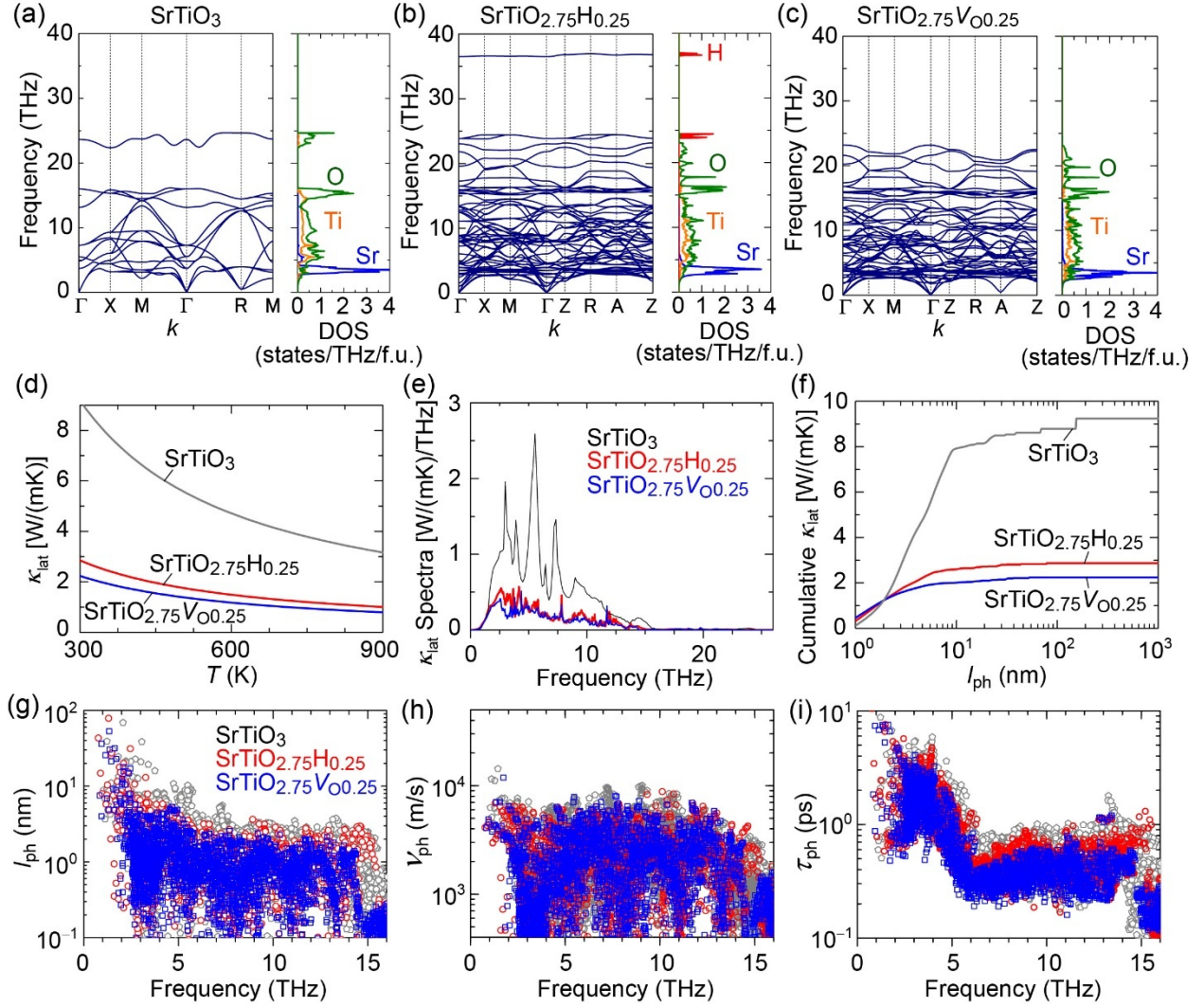


Figure 4. (a-c) Phonon dispersion (left panel) and partial phonon density of states (DOS) projected on each element (right panel) at $T = 300$ K for (a) cubic SrTiO_3 , (b) $\text{SrTiO}_{2.75}\text{H}_{0.25}$, and (c) $\text{SrTiO}_{2.75}\text{V}_{0.25}$ models. (d) T dependences of calculated κ_{lat} . (e) κ_{lat} spectra at $T = 300$ K. (f) Cumulative κ_{lat} as a function of phonon mean free path (l_{ph}). (g) l_{ph} , (h) phonon group velocity (v_{ph}), and (i) phonon lifetime (τ_{ph}) as a function of the phonon frequency.

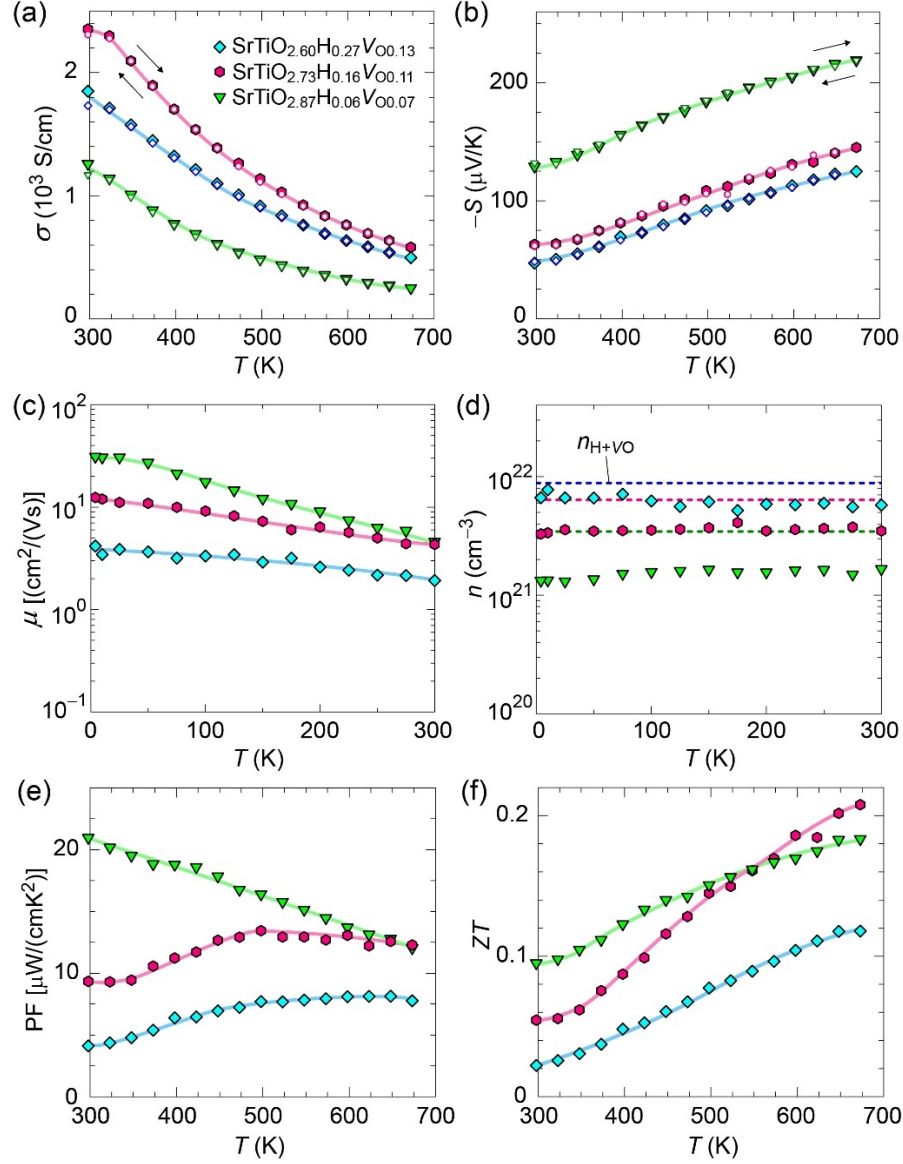
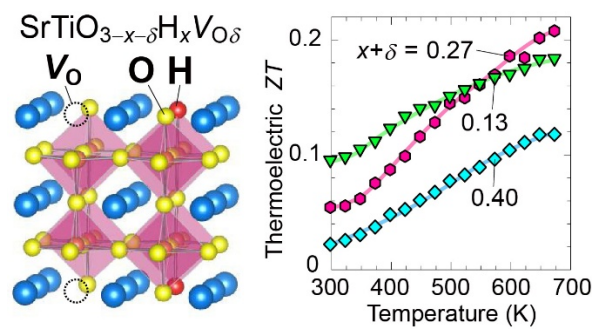


Figure 5. Thermoelectric properties for $\text{SrTiO}_{3-x}\text{H}_x\text{VO}_\delta$ bulks. (a,b) T dependences of (a) electrical conductivity (σ) and (b) Seebeck coefficient (S) at $T \geq 300$ K. The measurements were initially performed during the heating process (closed symbols), and then switched to the cooling process (open symbols). (c,d) T dependences of (c) Hall mobility (μ) and (d) carrier concentration (n) at $T \leq 300$ K. The dotted lines in (d) indicate the carrier concentration ($n_{\text{H+VO}}$) estimated by considering that all H^- provides one electron and VO provides two electrons in $\text{SrTiO}_{3-x}\text{H}_x\text{VO}_\delta$. (e,f) T dependences of (e) power factor (PF) and (f) dimension-less figure of merit (ZT).



For Table of Contents Only

Supporting Information

Strong phonon scattering and enhanced thermoelectric performance in SrTiO₃ polycrystals by simultaneous hydrogen substitution and oxygen vacancy formation

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Table S1. Crystallographic data obtained by Rietveld refinement results of NPD patterns for $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{VO}_\delta$ bulks.

Table S2. Crystallographic data obtained by Rietveld refinement results of NPD patterns for SrTiO_3 bulk.

Microstructure and chemical composition analysis

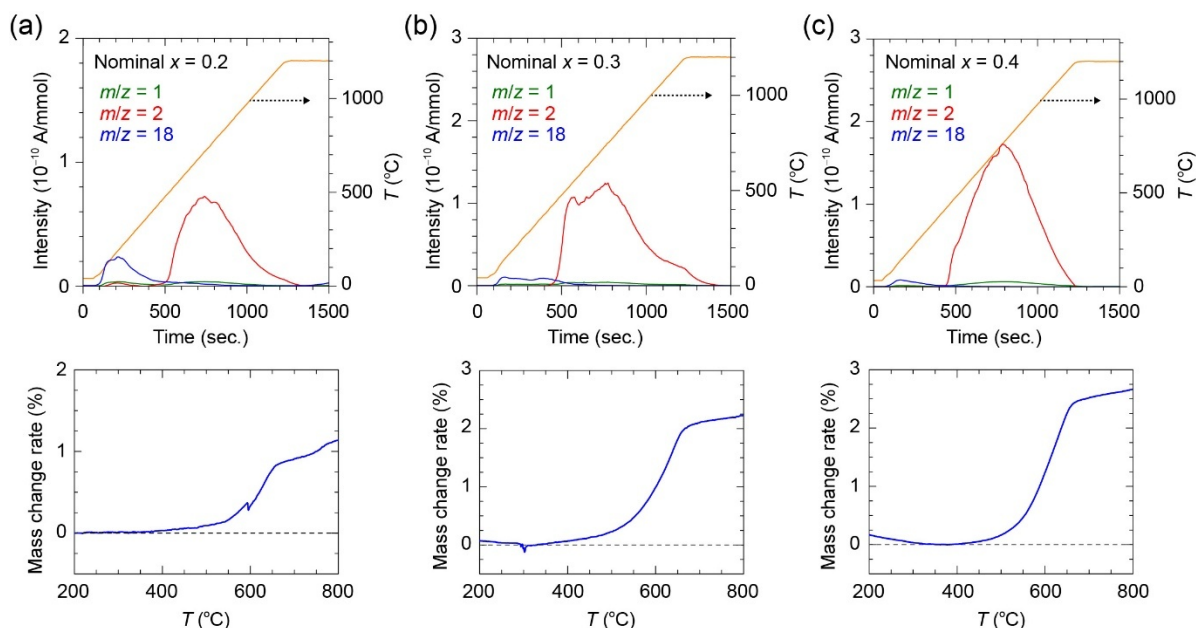


Figure S1. Thermal desorption spectroscopy (TDS) spectra for H ($m/z = 1$), H_2 ($m/z = 2$), H_2O ($m/z = 18$) and thermogravimetric analysis (TGA) spectra for $\text{SrTiO}_{3-x}\text{H}_x$ powders with nominal $x =$ (a) 0.2, (b) 0.3, and (c) 0.4.

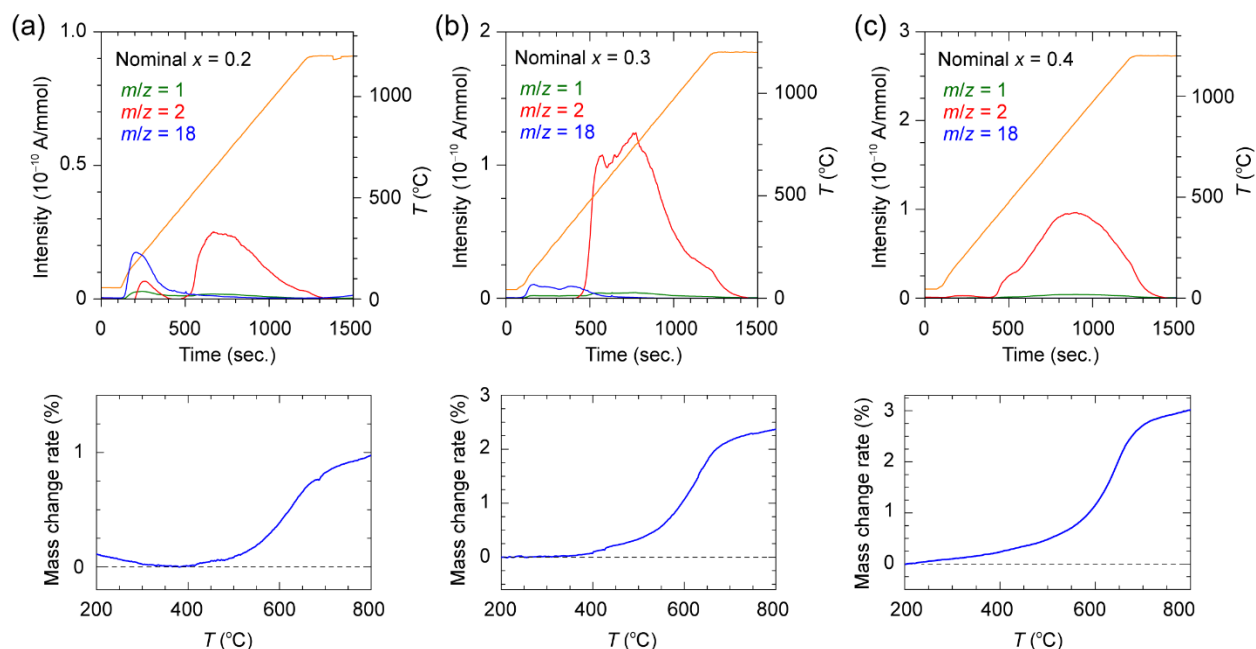


Figure S2. TDS spectra for H ($m/z = 1$), H_2 ($m/z = 2$), H_2O ($m/z = 18$) and TGA spectra for $\text{SrTiO}_{3-x}\text{H}_x/\text{V}_{0.8}$ bulks obtained by sintering $\text{SrTiO}_{3-x}\text{H}_x$ powders with nominal $x =$ (a) 0.2, (b) 0.3, and (c) 0.4.

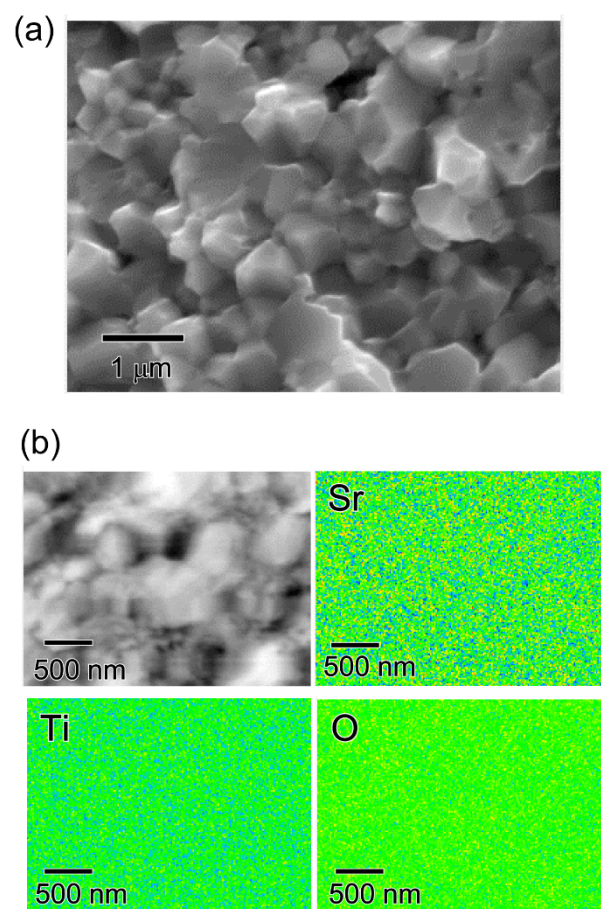


Figure S3. (a) Microstructure of broken-out surface and (b) chemical composition mappings of Sr, Ti, and O elements for the polished surface for $\text{SrTiO}_{2.73}\text{H}_{0.16}\text{V}_{\text{O}0.11}$ bulk.

Neutron diffraction measurements

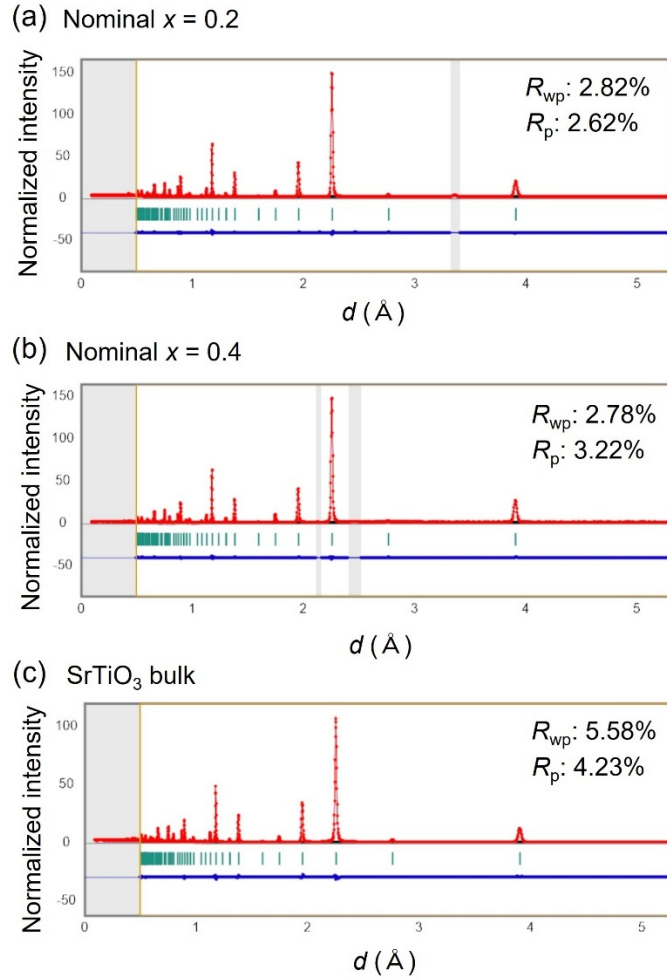


Figure S4. (a,b) Neutron powder diffraction (NPD) patterns for $\text{SrTiO}_{3-x}\text{H}_x\text{VO}_\delta$ bulks obtained by sintering $\text{SrTiO}_{3-x}\text{H}_x$ powders with nominal $x =$ (a) 0.2 and (b) 0.4, and (c) NPD pattern for SrTiO_3 bulk. The green tick marks and blue lines denote the Bragg peak positions from cubic SrTiO_3 structure (Space group: $Pm\bar{3}m$) and the difference curves, respectively.

Table S1. Crystallographic data obtained by Rietveld refinement results of NPD patterns for $\text{SrTiO}_{3-x}\text{H}_x\text{VO}_\delta$ bulks obtained by sintering $\text{SrTiO}_{3-x}\text{H}_x$ powders with nominal $x = 0.2$ and 0.4 . a , Occ., B (B_{11} and B_{33}) are the lattice parameter, the site occupancy, and anisotropic displacement parameters, respectively.

$\text{SrTiO}_{3-x}\text{H}_x\text{VO}_\delta$	Nominal $x = 0.2$		Nominal $x = 0.4$	
Crystal system	Cubic		Cubic	
Space group	$Pm\bar{3}m$		$Pm\bar{3}m$	
a (nm)	0.3908204(4)		0.3908404(4)	

Nominal $x = 0.2$						
	x	y	z	Occ.	$B_{11}(\text{\AA}^2)$	$B_{33}(\text{\AA}^2)$
Sr	0	0	0	0.994(1)	0.612(7)	
Ti	1/2	1/2	1/2	0.992(1)	0.412(9)	
O	0	1/2	1/2	0.9599(2)	0.884(8)	0.282(13)
H	0	1/2	1/2	0.0286(2)	$= B_{11}(\text{O})$	$= B_{33}(\text{O})$

Nominal $x = 0.4$						
	x	y	z	Occ.	$B_{11}(\text{\AA}^2)$	$B_{33}(\text{\AA}^2)$
Sr	0	0	0	1.000	0.693(7)	
Ti	1/2	1/2	1/2	0.973(2)	0.353(8)	
O	0	1/2	1/2	0.9069(4)	1.010(8)	0.230(12)
H	0	1/2	1/2	0.0759(6)	$= B_{11}(\text{O})$	$= B_{33}(\text{O})$

Table S2. Crystallographic data obtained by Rietveld refinement results of NPD patterns for SrTiO_3 bulk.

SrTiO_3						
Crystal system	Cubic					
Space group	$Pm\bar{3}m$					
a (nm)	0.3905431(2)					

	x	y	z	Occ.	$B_{11}(\text{\AA}^2)$	$B_{33}(\text{\AA}^2)$
Sr	0	0	0	1	0.502(3)	
Ti	1/2	1/2	1/2	0.985(1)	0.208(4)	
O	0	1/2	1/2	0.9998(4)	0.796(3)	0.161(5)

Phonon transport measurements

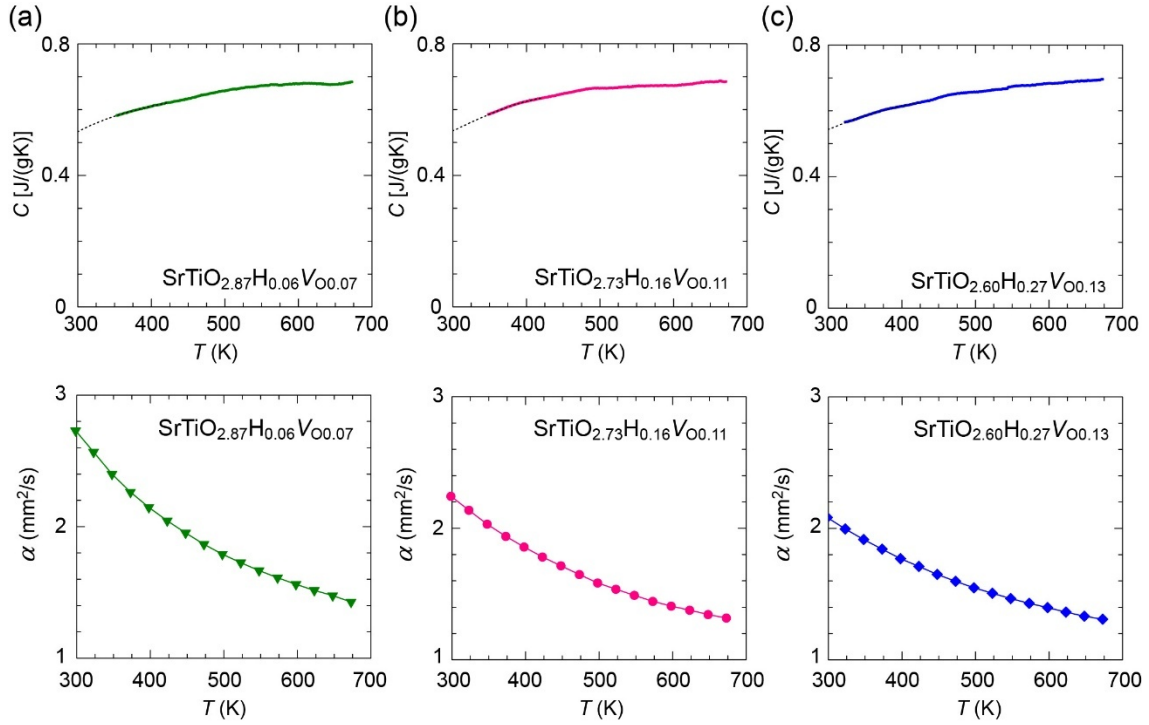


Figure S5. Temperature (T) dependence of heat capacity (C) and thermal diffusivity (D) for bulk samples of $\text{SrTiO}_{2.87}\text{H}_{0.06}\text{V}_{0.07}$, $\text{SrTiO}_{2.73}\text{H}_{0.16}\text{V}_{0.11}$, and $\text{SrTiO}_{2.60}\text{H}_{0.27}\text{V}_{0.13}$. The black dotted line in C vs. T data indicates the polynomial fitting with $C = aT^3 + bT^2 + cT + d$, where a , b , c , and d are fitting parameters.

DFT calculations

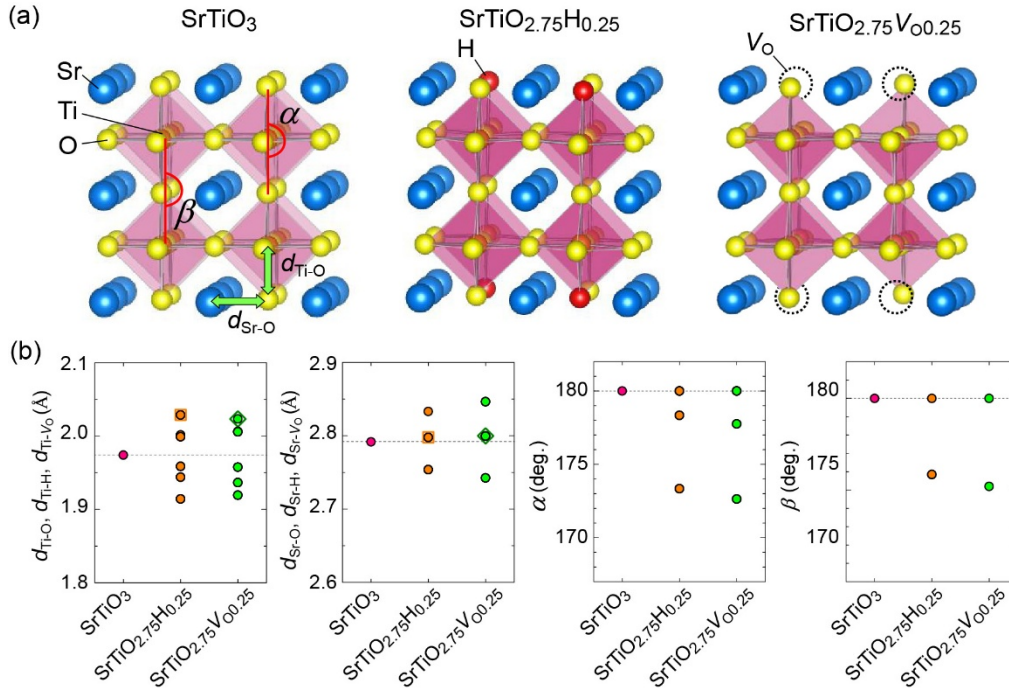


Figure S6. (a) Fully-relaxed crystal structures of cubic SrTiO_3 , $\text{SrTiO}_{2.75}\text{H}_{0.25}$, and $\text{SrTiO}_{2.75}\text{V}_{0.25}$ models, drawn by VESTA.¹ Sr, Ti, O, H atoms are depicted by blue, orange, yellow, and red spheres, respectively. V_O position is indicated by dotted circles. (b) Ti–(O,H, V_O) and Sr–(O,H, V_O) lengths (the circle, square, and diamond markers represent the lengths of Ti–O, Ti–H, and Ti– V_O , respectively), as well as (O,H, V_O)–Ti–(O,H, V_O) angles (α) in each Ti–(O,H, V_O)₆ octahedron and Ti–(O,H, V_O)–Ti angles (β) between two Ti–(O,H, V_O)₆ octahedra. The Ti– V_O length is determined by the distance between Ti and the center of V_O .

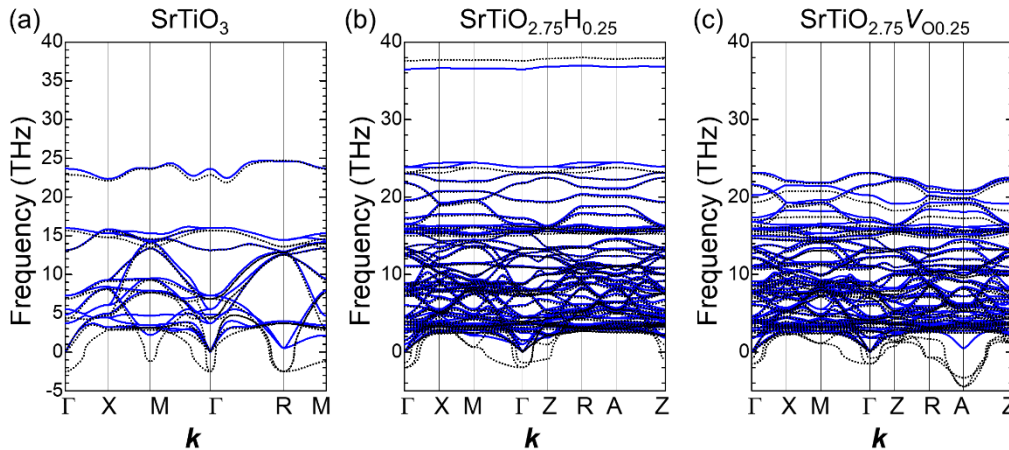


Figure S7. Comparison of harmonic phonon dispersion (black dot lines) and finite-temperature phonon dispersion at $T = 300$ K (blue solid lines) for (a) cubic SrTiO_3 , (b) $\text{SrTiO}_{2.75}\text{H}_{0.25}$, and (c) $\text{SrTiO}_{2.75}\text{V}_{0.25}$ models. When transferring the cubic SrTiO_3 (5 atoms) to tetragonal $\text{SrTiO}_{2.75}\text{H}_{0.25}$ and $\text{SrTiO}_{2.75}\text{V}_{0.25}$ cell (20 atoms), R(0.5 0.5 0.5) is transferred to Γ (0 0 0). The unstable phonon

mode originating from AFD rotation of Ti-O₆ octahedra is observed at R point for cubic SrTiO₃, while it is observed at Γ point for SrTiO_{2.75}H_{0.25}, and SrTiO_{2.75} V_{O0.25}. Note that the additional unstable phonon mode is observed at A point for SrTiO_{2.75} V_{O0.25}.

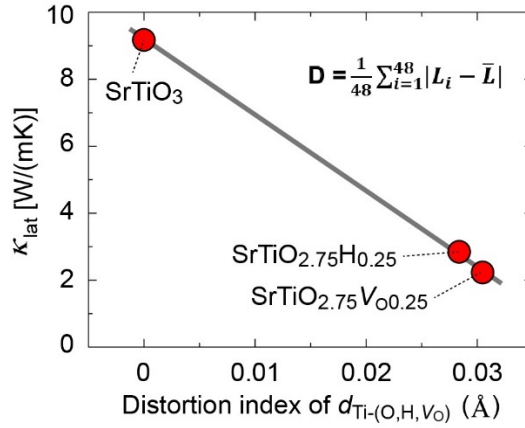


Figure S8. Relationship between the calculated κ_{lat} at $T = 300$ K and the deviation index (D) of Ti-(O,H, V_{O}) lengths for SrTiO₃, SrTiO_{2.75}H_{0.25}, and SrTiO_{2.75}V_{0.25} models. The distortion index D of perovskite oxides ABO_3 is evaluated by $D = \frac{1}{n} \sum_{i=1}^n |d_i - \bar{d}|$, where n is the number of B -O bonds, d_i is each B -O bond length and $\bar{d}$ is the average bond length in the B -O₆ polyhedra.²⁻⁴ The Ti- V_{O} length is determined by the distance between Ti and the center of V_{O} .

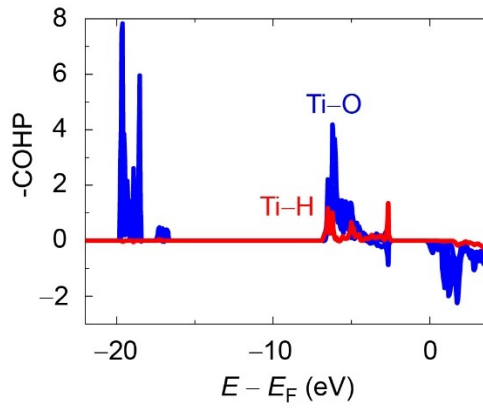


Figure S9. Calculated $-\text{COHPs}$ for Ti-O and Ti-H bonds in SrTiO_{2.75}H_{0.25} model. In SrTiO_{2.75}H_{0.25} model, there are 5 different Ti-O bonds due to the distortion. Therefore, we plot $-\text{COHPs}$ for all 5 Ti-O bonds. The positive value of $-\text{COHP}$ indicates the bonding state, while the negative value is the anti-bonding state. The $-\text{iCOHP}$ values were calculated by integrating $-\text{COHP}$ up to Fermi level (E_{F}) to estimate the bonding strength per bond. The averaged $-\text{iCOHP}$ value of Ti-O bond is 3.58 eV/bond, while that of Ti-H bond is only 0.96 eV/bond.

Carrier mobility analysis

Carrier mobility analyses were performed for $\text{SrTiO}_{2.87}\text{H}_{0.06}\text{V}_{0.07}$, $\text{SrTiO}_{2.73}\text{H}_{0.16}\text{V}_{0.11}$, and $\text{SrTiO}_{2.60}\text{H}_{0.27}\text{V}_{0.13}$ bulk samples. It is known that for electron-doped SrTiO_3 with $n > 10^{19} \text{ cm}^{-3}$, μ at T below 300 K is mainly dominated by electron–electron scattering.⁵ This is because the high carrier density effectively screens the contribution of optical phonon scattering. However, at higher T , the μ is primarily limited by scattering from longitudinal (LO) optical phonons.^{6–8} We then analyzed the contribution of each scattering on μ in $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{\delta}$ bulks. As shown in **Figures S10a-c**, we fitted the low- T Hall mobility (μ_{Hall}) using Matthiessen's rule: $\mu_{\text{tot}}^{-1} = \mu_{\text{imp.}}^{-1} + \mu_{\text{e-e}}^{-1} + \mu_{\text{opt.}}^{-1}$. Here, $\mu_{\text{imp.}}$ is the low- T limit of the μ determined by ionized impurity scattering, $\mu_{\text{e-e}}$ is the electron-electron scattering limited mobility, and $\mu_{\text{opt.}}$ is the optical phonon scattering limited mobility. Each mobility component is described as follows: $\mu_{\text{imp.}}^{-1} = A$ (constant), $\mu_{\text{e-e}}^{-1} = \alpha T^2$ (α is a measure of the strength of electron-electron scattering), and $\mu_{\text{opt.}}^{-1} = 1 / (B(\exp(\frac{\hbar\omega_0}{kT}) - 1))$, where B is constant, in the degenerate regime. The LO optical phonon energy ($\hbar\omega_0$) was fixed at 100 meV, which is typical for cubic SrTiO_3 .⁹ The calculated $\mu_{\text{tot.}}$ (shown as red line) based on the Matthiessen's rule matched experimental μ_{Hall} over a wide T range. The estimated $\mu_{\text{imp.}}$ decreases from 31 $\text{cm}^2/(\text{Vs})$ for $\text{SrTiO}_{2.87}\text{H}_{0.06}\text{V}_{0.07}$ to 3.8 $\text{cm}^2/(\text{Vs})$ for $\text{SrTiO}_{2.60}\text{H}_{0.27}\text{V}_{0.13}$. The decrease of μ with increasing T is mainly due to stronger electron-electron scattering. The estimated α for electron-electron scattering increases from $2.30 \times 10^{-6} \text{ Vs/cm}^2\text{K}^2$ for $\text{SrTiO}_{2.87}\text{H}_{0.06}\text{V}_{0.07}$ and $4.52 \times 10^{-6} \text{ Vs/cm}^2\text{K}^2$ for $\text{SrTiO}_{2.60}\text{H}_{0.27}\text{V}_{0.13}$. **Figure S10d** summarizes the H and V_O concentration ($x+\delta$) dependence of the $\mu_{\text{imp.}}$ (triangles) and $\mu_{\text{e-e}}$ (pentagons) calculated using the extracted fitting parameters, and $\mu_{\text{tot.}}$ (circles) at $T = 300 \text{ K}$. The higher concentration of H^- and V_O result in the

reduction both of $\mu_{\text{imp.}}$ and $\mu_{\text{e-e}}$ because of their contribution to the impurity scattering and increase of carrier concentrations.

We also estimated weighted carrier mobility (μ_w) at high $T \geq 300$ K using the equation: $\mu_w =$

$$\frac{3h^3\sigma}{8\pi(2m_e k_B T)^{3/2}} \left[\frac{\exp\left[\frac{|S|}{k_B/e} - 2\right]}{1 + \exp\left[-5\left(\frac{|S|}{k_B/e} - 1\right)\right]} + \frac{\frac{3}{\pi^2} \frac{|S|}{k_B/e}}{1 + \exp\left[5\left(\frac{|S|}{k_B/e} - 1\right)\right]} \right].$$

Here, h is the Planck constant, k_B is the

Boltzmann constant, e is the elementary electric charge, and m_e is the free electron mass.¹⁰ μ_w is

related to the drift mobility μ by $\mu_w \approx \mu \left(\frac{m^*}{m_e}\right)^{3/2}$, where m^* is the density of states effective mass.

Figures S10e-g show the high- T μ_w fitted using the Matthiessen's rule: $\mu_{\text{tot.}}^{-1} = \mu_{\text{imp.}}^{-1} + \mu_{\text{opt.}}^{-1}$. The

calculated $\mu_{\text{tot.}}$ (shown as red line) agrees well with the measured μ_w , indicating the μ is mainly

limited by the scattering from optical phonons at high T . **Figure S10f** shows the H and V_O

concentration ($x+\delta$) dependence of the $\mu_{\text{imp.}}$ (triangles) and $\mu_{\text{opt.}}$ (diamonds) calculated using the

extracted fitting parameters, and $\mu_{\text{tot.}}$ (circles) at $T = 673$ K. Both $\mu_{\text{imp.}}$ and $\mu_{\text{opt.}}$ decrease with

increase of $x+\delta$, indicating that higher impurity scattering and optical phonon scattering reduce the

$\mu_{\text{tot.}}$. From these results, the μ of the $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{O\delta}$ bulks is limited mainly by impurity scattering

and electron-electron scattering at low T and that is limited by optical phonon scattering at high T ,

similar to the $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ single crystal.¹ On the other hand, it is known that μ of conventional

La-doped SrTiO_3 polycrystals is often limited by strong grain boundary (GB) scattering.^{11,12} The

GBs act as a potential barrier for electron transport, reducing the σ across the GBs. In contrast, the

present samples exhibit significantly higher μ with minimal GB scattering across the entire T range.

This results in high PF by the single-crystal-like electron transport in $\text{SrTiO}_{3-x-\delta}\text{H}_x\text{V}_{O\delta}$ bulks even

with its polycrystal form.

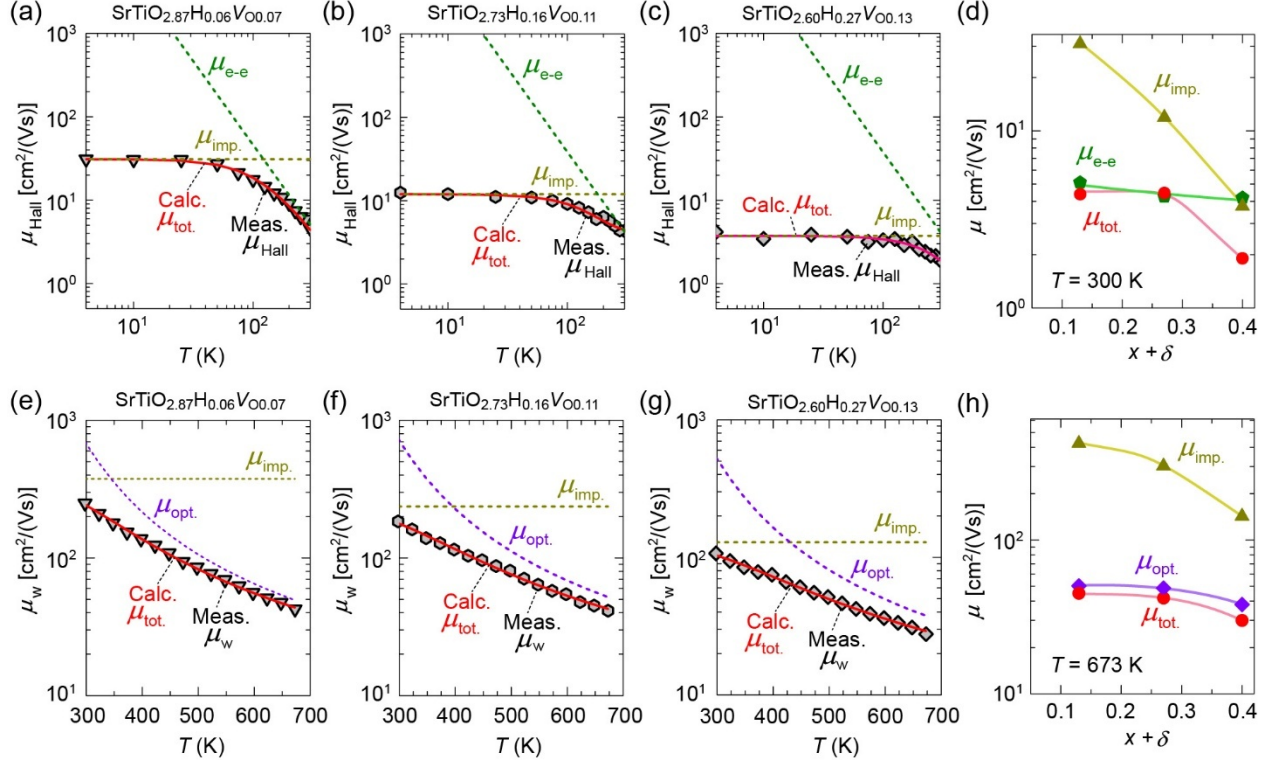


Figure S10. Analysis of carrier mobility (μ) as a function of temperature (T) for SrTiO_{2.87}H_{0.06}V_{0.07}, SrTiO_{2.73}H_{0.16}V_{0.11}, and SrTiO_{2.60}H_{0.27}V_{0.13} bulks. (a-c) Low- T Hall mobility (μ_{Hall}) vs. T (gray triangles). The red line shows the total mobility ($\mu_{\text{tot.}}$) calculated by Matthiessen's rule, $\mu_{\text{tot.}}^{-1} = \mu_{\text{imp.}}^{-1} + \mu_{\text{e-e}}^{-1} + \mu_{\text{opt.}}^{-1}$. The dark yellow, green, purple lines show the ionized impurity scattering limited mobility ($\mu_{\text{imp.}}$), the electron-electron scattering limited mobility ($\mu_{\text{e-e}}$), and the optical phonon scattering limited mobility ($\mu_{\text{opt.}}$), respectively. (d) H and V_{O} concentration ($x+\delta$) dependence of the $\mu_{\text{imp.}}$ (triangles) and $\mu_{\text{e-e}}$ (pentagons) calculated using the extracted fitting parameters, and $\mu_{\text{tot.}}$ (circles) at $T = 300$ K. (e-f) High- T weighted mobility (μ_w) vs. T (gray triangles). (h) H and V_{O} concentration ($x+\delta$) dependence of the $\mu_{\text{imp.}}$ (triangles) and $\mu_{\text{opt.}}$ (diamonds) calculated using the extracted fitting parameters, and $\mu_{\text{tot.}}$ (circles) at $T = 673$ K.

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