Thermoelectric properties of Nb-doped Sr$_{1-x}$(La$_{0.5}$Na$_{0.5}$)$_x$TiO$_3$ perovskites

Makoto Tachibana$^1$, Ahmad Rifqi Muchtar$^{1,2}$, and Takao Mori$^{1,2}$

$^1$International Center for Materials Nanoarchitechtonics, National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan
$^2$Institute of Technology Bandung, Bandung 40132, Indonesia

Received October 31, 2021; revised November 25, 2021; accepted December 14, 2021; published online December 23, 2021

We report the thermal conductivity ($\kappa$) and electrical conductivity ($\sigma$) of perovskite Sr$_{1-x}$(La$_{0.5}$Na$_{0.5}$)$_x$TiO$_3$ (0 $\leq$ $x$ $\leq$ 1) and the thermoelectric properties of Nb-doped samples for $x$ = 0.1 and 0.2. The $\kappa$ of the solid solution shows a distinct minimum near the cubic-tetragonal phase boundary at $x$ = 0.2, where the value becomes close to the minimum theoretical $\kappa$. Nb doping to $x$ = 0.2 retains the high power factor found in Nb-doped SrTiO$_3$, but also raises the $\kappa$ to result in a thermoelectric figure of merit of 0.24 at 773 K.

With such an objective in mind, this study reports the $\kappa$ of Sr$_{1-x}$(La$_{0.5}$Na$_{0.5}$)$_x$TiO$_3$ solid solutions (0 $\leq$ $x$ $\leq$ 1) and examines the thermoelectric properties of Nb-doped samples for $x$ = 0.1 and 0.2. The solid solution, referred to as SLNTO in this paper, shows changes in crystal structure from cubic (space group $Pm\bar{3}m$) to tetragonal ($I4/mcm$) at $x$ $\approx$ 0.2–0.3, and then to rhombohedral ($R3$) at $x$ $\approx$ 0.7–0.8.

Unexpectedly, we find anomalously low $\kappa$ for $x$ = 0.2, which is even smaller than the value found in LTNTO. We also find that Nb doping to $x$ = 0.2 retains the high power factor of Nb-doped STO but considerably raises the lattice $\kappa$ from the undoped composition. As the results suggest that strong phonon damping is realized near a structural phase boundary, further control in composition may lead to a very high $ZT$ in this important system.

Polycrystalline samples of SLNTO ($x$ = 0, 0.1, 0.2, 0.5, 1) and those with 10% of Ti replaced by Nb for $x$ = 0.1 and 0.2 were prepared by solid-state reactions. Dried powders of SrCO$_3$ (99.99%), La$_2$O$_3$ (99.99%), Na$_2$CO$_3$ (99.99%), TiO$_2$ (99.99%), and Nb$_2$O$_5$ (99.99%) were mechanically ground and calcined at 1273 K in air for 6 h in alumina crucibles. The calcined powders were then ball milled for 20 h and uniaxially pressed into pellets, which were fired at 1423 K in air for 10 h. To prevent evaporation loss of Na, the pellets of all samples except $x$ = 0 were buried in sacrificial powder of the same composition. The fired pellets were ball milled again and pressed into pellets under an isostatic pressure of 200 MPa, using a cold isostatic press. The final sintering conditions were: (1) for SLNTO (except $x$ = 0) without Nb doping, pellets were buried in sacrificial powder and sintering at 1623 K in air for 10 h. (2) For $x$ = 0, pellets were sintering at 1773 K in air for 10 h. (3) For the Nb-doped samples, pellets were buried in carbon powder placed in alumina crucibles, which provided reducing condition during sintering at 1623 K for 10 h. For each sample, the final pellet density was >93% of theoretical value. X-ray powder diffraction using Cu K$\alpha$ radiation confirmed the phase purity of each sample, and the obtained lattice parameters for SLNTO agreed well with those reported previously.
Thermal conductivity \( \kappa \) was determined from thermal diffusivity \( D \), heat capacity \( C_p \), and density \( \rho \), through the relation \( \kappa = D \rho C_p \). Thermal diffusivity was measured in nitrogen atmosphere by the flash technique, using Netzsch LFA 467. For the measurements, 8 \( \times \) 8 mm square plates of \( \sim 2 \) mm thickness were coated on both sides with thin layer of graphite. \( C_p \) values were also derived with LFA 467 using a reference sample of Pyroceram 9606. For SLNTO \( (0 \leq x \leq 1) \) without Nb doping, the \( C_p \) values were checked by comparison with the weighted average of the reported \( C_p \) values for STO and LNTO.\(^{5,8}\) As the present data agreed within 15% with such values but showed larger scatter, we used the weighted average \( C_p \) values for \( \kappa \) calculation. For the Nb-doped samples, we used the \( C_p \) data directly obtained with LFA 467. Electrical conductivity \( \sigma \) and Seebeck coefficient \( S \) of bar-shaped samples were measured under helium atmosphere using Advance Riko ZEM-3.

The results of \( \kappa \) measurements for SLNTO \( (0 \leq x \leq 1) \) are shown in Fig. 1. As these samples are insulators, \( \kappa \) corresponds to lattice \( \kappa \). The values for \( x = 0 \) and 1 are in good agreement with the reported data\(^{5,8}\) \( x = 0 \) shows a typical crystalline \( T^{-1} \) dependence due to the anharmonic interactions of phonon-phonon Umklapp scattering, while \( x = 1 \) exhibits nearly \( T \)-independent glasslike behavior. As shown previously,\(^{5,8}\) the values for \( x = 1 \) are close to the minimum theoretical \( \kappa \) \( (\kappa_{\text{min}}) \) for STO,\(^{5,8}\) which has been calculated using the Cahill’s model\(^{14}\) and reproduced in Fig. 1. \( \kappa_{\text{min}} \) corresponds to heat transport via random walk of energy between localized, uncorrelated oscillators, and describes the \( \kappa \) of amorphous solids and highly disordered crystals.\(^{14}\) For \( x = 0.1 \) and 0.5, the \( \kappa \) values are intermediate between \( x = 0 \) and 1, transforming from crystalline to glasslike behavior with increasing \( x \). On the other hand, \( x = 0.2 \) shows unexpectedly small \( \kappa \), even smaller than \( x = 1 \) and almost coinciding with \( \kappa_{\text{min}} \) at the highest temperature. This small \( \kappa \) was fully reproduced on another sample from a different batch, confirming that it is an intrinsic property of this composition. The inset of Fig. 1 presents the \( \kappa \) values of each composition at 473 K, along with the phase boundaries\(^{10}\) of the cubic \( Pm\bar{3}m \) to tetragonal \( I4/mcm \) transition and \( I4/mcm \) to rhombohedral \( R3 \) \( \kappa \) transition. The transition from cubic to tetragonal is the same as that occurs on cooling for \( x = 0 \) (STO) at 105 K, and is characterized by cooperative tilting of TiO\(_6\) octahedra in a staggered manner along the cubic (001) direction.\(^{15}\) This second-order transition is accompanied by the softening of optic phonons at the cubic \( R \)-point zone boundary,\(^{15}\) and the dip in \( \kappa \) for STO around the 105 K transition\(^{15}\) has been attributed to strong damping of heat-carrying acoustic phonons due to interactions with the soft optic phonons.\(^{17}\) As the composition \( x = 0.2 \) is located in the vicinity of this transition, it is likely that similar phonon damping mechanism is operative in \( x = 0.2 \) to suppress \( \kappa \). Indeed, similar features have been reported for GeTe and Pb\(_{1-x}\)Ge\(_x\)Te,\(^{18-20}\) the former showing a pronounced dip in \( \kappa \) at its ferroelectric transition, and the latter exhibiting minimum \( \kappa \) behavior at the composition \( x \approx 0.5 \) where the ground-state structure transforms from paraelectric to ferroelectric.\(^{20}\) Although Pb\(_{1-x}\)Ge\(_x\)Te is different from SLNTO in that the soft mode is located at the zone center, rather than at the zone boundary, either soft mode should couple with heat-carrying acoustic phonons to suppress \( \kappa \) as the phase transition is approached.

Having found anomalously low \( \kappa \) at \( x = 0.2 \), we now shift our focus to Nb-doped SLNTO. In this study, 10% of Ti was substituted with Nb, as this doping level often leads to peak \( \sigma \) values in power factor for STO-based materials.\(^{12,21}\) In Fig. 2, the \( \kappa \) of Nb-doped \( x = 0.1 \) and 0.2 are compared to those of undoped samples. Focusing first on \( x = 0.1 \) (shown with red square symbols), we find that the Nb-doped sample has slightly higher \( \kappa \) than that of undoped sample, with the difference at 323 K of 1 W m\(^{-1}\) K\(^{-1}\) gradually closing in with increasing temperature. As shown in the figure, this excess \( \kappa \) corresponds well with the extra electronic contribution \( \kappa_{\text{elec}} \) in the Nb-doped sample, which was calculated using the Wiedemann–Franz law \( \kappa_{\text{elec}} = \sigma LT \) (where \( L \) is the
Lorenz number $2.44 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$ and $\sigma$ is shown in Fig. 4). Such a good agreement implies that Nb doping does not significantly modify the phonon transport in $x=0.1$.

On the other hand, Nb doping leads to more unexpected result for $x=0.2$ (blue triangular symbols). Here, the difference between the Nb-doped and undoped samples is much larger than $\kappa_{\text{elct}}$ indicating significant modification in phonon transport. Moreover, the similarity in $\kappa$ between the Nb-doped samples of $x=0.1$ and $0.2$ suggests that Nb doping into $x=0.2$ eliminates the strong phonon damping that was present in the previous sample. This is very different from the case of $x=1$ (LNTO), where the glasslike $\kappa$ values are maintained with Nb doping. A likely explanation for this is that Nb doping to $x=0.2$ displaces the sample away from the cubic-tetragonal phase boundary, leading to the recovery of normal $\kappa$ value.

To explore this scenario, we discuss the crystal structure of Nb-doped $x=0.1$ and $0.2$. In perovskite $\text{ABO}_3$ with the ionic radii of $r_{\text{A}}, r_{\text{B}},$ and $r_{\text{O}}$, the ideal cubic $\text{Pm}\overline{3}m$ structure is found when the Goldschmidt tolerance factor $t = (r_{\text{A}} + r_{\text{O}})/\sqrt{2(r_{\text{B}} + r_{\text{O}})}$ is close to 1. The stoichiometric $\text{SrTiO}_3$, having $t=1.002$, is one such example. When the average size of A-site ions becomes small and $t<1$, the lattice adjusts to the mismatch of A–O and B–O bond lengths by cooperatively tilting the $\text{BO}_6$ octahedra. The tetragonal $I4/mcm$ phase in SLNTO ($0.2 < x < 0.8$) is one such example, and it is manifested in the X-ray powder diffraction pattern as the presence of new superlattice reflections and splitting of some of the main Bragg reflections. In Fig. 3, the powder pattern for tetragonal $x=0.5$ indeed shows (i) a weak superlattice reflection at $38.5^\circ$, which is at the $R$ point with the index of $32 1/2 1/2$ in the pseudocubic cell, and (ii) broadening of the cubic 220 peaks (from $K_{\text{O1}}$ and $K_{\text{O2}}$ reflection) at $\sim68^\circ$, as compared to the corresponding peaks for the undoped $x=0.1$ and $0.2$ in the cubic phase. The fact that the cubic 220 is not split cleanly into tetragonal 200 and $112$ (Ref. 22) in $x=0.5$ can be attributed to the small degree of tetragonal distortion and the relatively poor resolution of the present measurements.

When Nb is doped into SLNTO, the substitution of $\text{Nb}^{5+}$ for $\text{Ti}^{4+}$ creates $\text{Ti}^{1+}$. As both $\text{Nb}^{5+}$ and $\text{Ti}^{3+}$ are larger than $\text{Ti}^{4+}$ ($r_{\text{Nb}}^{5+}=0.64 \text{Å}$, $r_{\text{Ti}}^{3+}=0.67 \text{Å}$, and $r_{\text{Ti}}^{4+}=0.605 \text{Å}$, after Ref. 23), Nb doping is accompanied by a reduction in $t$ and an increase in the lattice parameter. As shown in Fig. 3, Nb doping to $x=0.1$ shifts the cubic 220 to a lower angle, reflecting the increase in cubic lattice parameter. Because the Nb doping does not create superlattice reflections nor change the 220 peak shape, the cubic symmetry is clearly maintained in Nb-doped $x=0.1$. On the other hand, Nb doping to $x=0.2$ broadens the 220 peaks into a shape that is strikingly similar to that of $x=0.5$, though the present data do not reveal discernible superlattice reflections. Therefore, the data suggest weak tetragonal distortion, but proper structural refinement based on synchrotron X-ray or neutron diffraction data would be needed to establish the true crystal symmetry. Tetragonal symmetry for this composition is also consistent with the tolerance factor: the Nb doping to $x=0.2$ reduces $t$ from 0.997 to 0.992, where the latter value is smaller than 0.9955 found for tetragonal $x=0.3$ ($r_{\text{Sr}}^{2+}=1.44 \text{Å}$, $r_{\text{La}}^{3+}=1.36 \text{Å}$, and $r_{\text{Na}}^{+}=1.39 \text{Å}$, after Ref. 23). Therefore, these considerations suggest that the Nb doping to $x=0.2$ displaces the sample away from the cubic-tetragonal phase boundary and likely into the tetragonal phase.

Finally, Fig. 4 shows the electronic transport properties and $\text{ZT}$ values for the Nb-doped $x=0.1$ and $0.2$. Corresponding data for 10% Nb-doped $x=0$ and 1,8,12 which have the same nominal carrier concentration, are also shown. For each sample, $\sigma$ and $S$ are typical of donor-substituted STO-based materials, where the $\text{Nb}^{5+}$ substitution for $\text{Ti}^{4+}$ creates $\text{Ti}^{1+}$ to fill the n-type conduction band. As for the power factor $S^2\sigma$, the most remarkable feature is that $x=0.1$ and $0.2$ retain the high value of $x=0$; this suggests that small replacement of $\text{Sr}^{2+}$ by $\text{La}^{3+}/\text{Na}^+$ does not significantly disrupt the electronic transport.
The ZT values at 773 K for the \( x = 0.1 \) and 0.2 samples are 0.26 and 0.24, respectively. Although \( x = 1 \) has a low power factor, its glasslike small \( \kappa \) (Ref. 8) leads to ZT that is nearly comparable to the others. The sample of \( x = 0 \) studied by Zhang et al.\(^1,2\) shows slightly smaller \( \kappa \) (4.5 W m\(^{-1}\) K\(^{-1}\) at 500 K) than \( x = 0.1 \) and 0.2, resulting in higher ZT. Here we note that if the very low lattice \( \kappa \) of undoped \( x = 0.2 \) is maintained upon Nb doping, ZT will be roughly twice as much as the present \( x = 0.1 \) and 0.2 values. Such a value would become the current state-of-the-art for STO-based materials.\(^3\)

In conclusion, we find very low \( \kappa \) near the cubic-tetragonal phase boundary at \( x = 0.2 \) in SLNTO, demonstrating that structural phase boundaries can be utilized to suppress \( \kappa \) in thermoelectric materials. As Nb doping to \( x = 0.2 \) retains the high power factor found in Nb-doped STO, further control in composition (such as tuning both \( x \) and Nb doping level to place the sample near the phase boundary) may lead to a combination of high power factor and low \( \kappa \), resulting in very high ZT.

Acknowledgments This study was supported by the funding from JST-Mirai JPMJMI19A1 and JSPS KAKENHI 19H00833. A. R. M. acknowledges NIMS-ICGP program for the Indonesia-Japan mobility grant.

ORCID IDs

Makoto Tachibana \( \text{https://orcid.org/0000-0002-5907-5563} \)
Takao Mori \( \text{https://orcid.org/0000-0003-2682-1846} \)

1) L. E. Bell, Science \( 321, \) 1457 (2008).
2) K. Koumoto, Y. Wang, R. Zhang, A. Kosuga, and R. Funahashi, Annu. Rev. Mater. Res. \( 40, \) 363 (2010).
3) X.-L. Shi, H. Wu, Q. Liu, W. Zhou, S. Lu, Z. Shao, M. Dargusch, and Z.-G. Chen, Nano Energy \( 78, \) 105195 (2020).
4) T. Okuda, K. Nakanishi, S. Miyasaka, and Y. Tokura, Phys. Rev. B \( 63, \) 113104 (2001).
5) Y. Wang, K. Fujimami, R. Zhang, C. Wan, N. Wang, Y. Ba, and K. Koumoto, Appl. Phys. Express \( 3, \) 031101 (2010).
6) S. R. Popuri, A. J. M. Scott, R. A. Downie, M. A. Hall, E. Suard, R. Decourt, M. Pollet, and J.-W. G. Bos, RSC Adv. \( 4, \) 33720 (2014).
7) Z. Lu, H. Zhang, W. Lei, D. C. Sinclair, and I. M. Reaney, Chem. Mater. \( 28, \) 925 (2016).
8) L. M. Daniels, S. N. Savvin, M. J. Pitcher, M. S. Dyer, J. B. Claridge, S. Ling, B. Slater, F. Corà, J. Alaria, and M. J. Rosseinsky, Energy Environ. Sci. \( 10, \) 1917 (2017).
9) R. Garg, A. Senyshyn, H. Boysen, and R. Ranjan, J. Phys. Condens. Matter \( 20, \) 505215 (2008).
10) R. H. Mitchell, A. R. Chakhmouradian, and P. M. Woodward, Phys. Chem. Minerals \( 27, \) 583 (2000).
11) L. M. Daniels, S. Ling, S. N. Savvin, M. J. Pitcher, M. S. Dyer, J. B. Claridge, B. Slater, F. Corà, J. Alaria, and M. J. Rosseinsky, J. Mater. Chem. A \( 6, \) 15640 (2018).
12) B. Zhang, J. Wang, T. Zou, S. Zhang, X. Yaer, N. Ding, C. Liu, L. Miao, Y. Li, and Y. Wu, J. Mater. Chem. C \( 3, \) 11406 (2015).
13) D. de Ligny and P. Richet, Phys. Rev. B \( 53, \) 3013 (1996).
14) D. G. Cahill, S. K. Watson, and R. O. Pohl, Phys. Rev. B \( 46, \) 6131 (1992).
15) G. Shirane and Y. Yamada, Phys. Rev. \( 177, \) 858 (1969).
16) V. Martelli, J. L. Jimenez, M. Continentino, E. Baggio-Saitovitch, and K. Behnia, Phys. Rev. Lett. \( 120, \) 125901 (2018).
17) H. H. Barrett, in Physical Acoustics, ed. W. P. Mason and R. N. Thurston (Academic, New York, 1970), Vol. VI, p. 65.
18) J. Li, Z. Chen, X. Zhang, Y. Sun, J. Yang, and Y. Pei, NPJ Asia Mater. \( 9, \) 1353 (2017).
19) X. Zhang, Z. Bu, S. Lin, Z. Chen, W. Li, and Y. Pei, Joule \( 4, \) 986 (2020).
20) R. M. Murphy, É. D. Murray, S. Fahy, and I. Savić, Phys. Rev. B \( 95, \) 144302 (2017).
21) A. V. Kovalevsky, M. H. Aguirre, S. Populoh, G. S. Patricio, N. M. Ferreira, S. M. Mkhalele, D. P. Fagg, A. Weidenkaff, and J. R. Frade, J. Mater. Chem. A \( 5, \) 3909 (2017).
22) R. H. Mitchell, Perovskites: Modern and Ancient (Almaz Press, Ontario, 2002).
23) R. D. Shannon, Acta Cryst. A \( 32, \) 751 (1976).