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Role of phonon scattering by elastic strain field in thermoelectric $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_{3-\delta}$

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Perovskite-type $\text{SrTiO}_{3-\delta}$ ceramics are multifunctional materials with significant potential as n-type thermoelectric (TE) materials. The electronic and thermal transport properties of spark plasma sintered polycrystalline $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_{3-\delta}$ ($x = 0.05, 0.075, 0.1$) ceramics are systematically investigated from (15–800) K. The $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$ simultaneously exhibits a large Seebeck coefficient, $\alpha > -80 \mu\text{V/K}$ and moderately high electrical resistivity, $\rho \sim 0.8 \text{ m}\Omega\text{-cm}$ at a carrier concentration of $\sim 10^{21} \text{ cm}^{-3}$ at 300 K resulting in a high TE power factor defined herein as $(\alpha^2 \sigma T) \sim 0.84 \text{ W/m-K}$ at 760 K. Despite the similar atomic masses of Sr (87.6 g/mol) and Y (88.9 g/mol), the lattice thermal conductivity (κ_L) of $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_{3-\delta}$ is significantly reduced with increased Y-doping, owing to the smaller ionic radii of Y^{3+} ($\sim 1.23 \text{ \AA}$, coordination number 12) compared to Sr^{2+} ($\sim 1.44 \text{ \AA}$, coordination number 12) ions. In order to understand the thermal conductivity reduction mechanism, the κ_L in the $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_{3-\delta}$ series are phenomenologically modeled with a modified Callaway's equation from 30–600 K. Phonon scattering by elastic strain field due to ionic radii mismatch is found to be the prominent scattering mechanism in reducing κ_L of these materials. In addition, the effect of Y-doping on the elastic moduli of $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_{3-\delta}$ ($x = 0, 0.1$) is investigated using resonant ultrasound spectroscopy, which exhibits an anomaly in $x = 0.1$ in the temperature range 300–600 K. As a result, the phonon mean free path is found to be further reduced in the $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$ compared to that of $\text{SrTiO}_{3-\delta}$, resulting in a considerably low thermal conductivity $\kappa \sim 2.7 \text{ W/m-K}$ at 760 K. Finally, we report a thermoelectric figure of merit (ZT) ~ 0.3 at 760 K in the $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$, the highest ZT value reported in the Y-doped SrTiO_3 ceramics thus far. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4882377>]

I. INTRODUCTION

Perovskite-type SrTiO_3 are versatile materials that exhibit novel transport properties namely, quantum paraelectricity,¹ induced ferroelectricity,^{2–4} superconductivity,⁵ coexistence of superconductivity and ferromagnetism,⁶ piezoelectricity,⁷ photo-catalytic activity,^{8,9} and potential thermoelectricity.¹⁰ The crystal structure of pure SrTiO_3 exhibits a cubic lattice ($a \sim 3.905 \text{ \AA}$, space group $Pm\bar{3}m$ at room temperature), with unit cell consisting of a titanium-oxygen (TiO_6) octahedron enclosed in a cube of Sr-atoms.¹¹ Below 105 K, SrTiO_3 undergoes a structural phase transition (SPT) from a cubic to tetragonal structure that is due to the rotation of the TiO_6 octahedra.¹² Carrier doping effects on the rotation of TiO_6 octahedra in SrTiO_3 were investigated by first-principle calculations by Uchida *et al.*,¹³ pointing out that further instabilities of the high temperature cubic phase could be induced by electron dopants of dissimilar atomic masses or radii. Despite the

simplicity of the crystal structure, the $\text{SrTiO}_{3-\delta}$ system exhibits a wide range of novel properties arising from small distortions of the ideal perovskite structure, due to light doping, defects, and/or oxygen non-stoichiometry.

In recent years, doped $\text{SrTiO}_{3-\delta}$ ceramics have attracted significant attention as potential n-type thermoelectric (TE) materials to couple with high TE performance of p-type Co-oxide based materials for use in a TE module.^{10,14} Pure SrTiO_3 is a wide band gap insulator ($E_g \sim 3.2 \text{ eV}$),^{15–17} which transforms into a degenerate semiconductor upon doping at the Sr-site, or Ti-site and/or creating oxygen vacancies. Oxygen vacancies play an important role in ceramic oxides, in enhancing electronic properties as well as acting as scattering centers in order to reduce thermal conductivity. They are known to create defect states near the conduction band that enhance the electrical conductivity in the non-stoichiometric $\text{SrTiO}_{3-\delta}$.¹⁸ Further, the role of oxygen vacancies in suppressing the thermal diffusivity of reduced rutile TiO_2 was theoretically pointed out by Klemens.¹⁹ The doped $\text{SrTiO}_{3-\delta}$ simultaneously exhibits high Seebeck coefficients ($\alpha \sim -200$ – $300 \mu\text{V/K}$ at 750 K) originating from large

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effective masses (m^*) of the carrier electrons (~ 6 – 10) m_e , and moderately low electrical resistivities ($\rho < 5$ m Ω -cm at 750 K), which give rise to high thermoelectric power factors ($PF = \alpha^2 \sigma T \sim 0.8$ – 1.3 W/m-K).^{10,20} They are chemically stable, non-toxic perovskite oxides, ideal for application as TE device at moderate to high temperature ranges. Unlike many doped semiconductors, however, one of the chief advantages of the doped $\text{SrTiO}_{3-\delta}$ is the non-existence of bipolar contribution (i.e., minority carriers) in electrical transport properties at higher temperatures. Based on the estimation of n-type and p-type pinning energies, Robertson *et al.*²¹ pointed out that the doped SrTiO_3 oxides are unlikely to form bipolar semiconductors by electronic doping, due to their high p-type pinning limits in TiO_2 and SrTiO_3 . This gives rise to comparatively high electronic transport properties at temperatures, $T > 600$ K, without any bipolar contribution.

Despite the promising electronic properties of $\text{SrTiO}_{3-\delta}$ ceramics, a comparatively high total thermal conductivity, $\kappa_T \sim 11$ W/m-K at 300 K in single crystalline SrTiO_3 ,²² is observed owing to their simple cubic structure and bonding with lighter oxygen atoms.¹⁰ To enhance the thermoelectric figure-of-merit (ZT) or $ZT = \frac{\alpha^2 \sigma T}{\kappa_L + \kappa_E}$, the challenge is to reduce the high κ_T ($= \kappa_E + \kappa_L$) arising from a considerably large κ_L , while simultaneously maintaining their promising electronic transport properties. The Y-doped SrTiO_3 ceramics have been studied extensively for their potential as anode/cathode materials for solid oxide fuel cells (SOFCs), where high electronic conductivity is required.^{23–25} Hui *et al.*²⁶ reported “unusually high” electrical conductivity ($\sigma \sim 64$ S/cm) in the $\text{Sr}_{0.88}\text{Y}_{0.08}\text{TiO}_3$ at 800 C, in comparison ($\sigma < 20$ S/cm) to other rare earth dopants such as La, Pr, Sm, Gd, and Yb. The difference in electronic structures between Y:[Kr]4d5s² and other rare-earth elements, with the exception of La:[Xe]5d6s², is the absence of the f-shell electrons that may lead to different electron scattering mechanisms. In the hot-pressed $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_3$ ceramic, a high thermoelectric power factor $PF \sim 0.7$ W/m-K at 750 K is reported by Obara *et al.*,²⁷ although a thermal conductivity $\kappa_T \sim 5.7$ W/m-K at 490 K consequently reduces the thermoelectric ZT to about 0.1 at 490 K. Our interest in the Y-doped $\text{SrTiO}_{3-\delta}$ lies in the promising electronic transport properties and a potentially low thermal conductivity, arising from the smaller ionic radii of Y^{3+} (~ 1.23 Å, coordination number 12) compared to Sr^{2+} (~ 1.44 Å, coordination number 12) ions.²⁸ This value of ionic radii of Y^{3+} of coordination number (CN) 12, is linearly extrapolated from Shannon *et al.*,²⁸ in the absence of ionic radii value at a CN ~ 12 . Our research indicates that the electronic transport properties of Y-doped as well as Yb-doped $\text{SrTiO}_{3-\delta}$ are highly dependent on synthesis parameters.²⁹ A systematic optimization of synthesis conditions yields a high power factor ($\alpha^2 \sigma T$) $PF \sim 0.84$ W/m-K and a comparatively low thermal conductivity, $\kappa_T \sim 2.7$ W/m-K at 760 K, resulting in a high $ZT \sim 0.3$ at 760 K in the $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_3$.

II. EXPERIMENTAL PROCEDURE

Polycrystalline $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_{3-\delta}$ ($x = 0, 0.05, 0.075, 0.1$) ceramics were synthesized using combined solid-state reaction (SSR) in air and rapid densification via a specified spark

plasma sintering (SPS) technique. Stoichiometric ratios of SrCO_3 (Sigma Aldrich, 99.9%), TiO_2 (Sigma Aldrich, nano-powders < 20 nm, 99.5% purity), and Y_2O_3 (Alfa Aesar, 99.9%) powders were mixed according to the following conventional SSR:

The mixed powders were finely ground by a mortar and pestle, cold pressed, and then calcined in air at 1300 °C, close to the melting point of SrCO_3 (~ 1350 °C). The process is followed by intermediate grinding and cold pressing and further calcinations at 1400 °C a few more times. The calcined powders were rapidly densified by SPS under dynamic vacuum using Dr. SINTER LAB 515S system. The SPS yields a highly densified compact pellet, with a density (ρ_D) as measured using the Archimedes principle that is $>95\%$ of the theoretical density of the material. The as-produced pellets are 12.7 mm in diameter and 2–3 mm thick. The SPS processed samples do not show any anisotropy in transport properties due to the cubic structure of SrTiO_3 crystal lattice. High resolution X-ray diffraction (HR-XRD) is performed using a RIGAKU Ultima IV diffractometer, $\text{Cu K}\alpha$ radiation, $\lambda = 1.5406$ Å on samples densified using SPS. Quantitative analysis using Rietveld refinement is performed on the XRD peaks using PDXL software.

Resistivity and thermopower were measured quasi-simultaneously in a closed cycle helium cryostat from 10 to 300 K and the 4-probe measurement technique is described in detail elsewhere.³⁰ The commercial ZEM (ULVAC-RIKO, ZEM-2) was used to measure resistivity and thermopower from 300–800 K under partial He-atmosphere. Thermal conductivity was measured from 10 to 300 K on a custom designed measurement system using steady state technique.³¹ The thermal conductivity at low temperatures is corrected for radiation losses above 200 K, using the Stefan-Boltzmann power law.³¹ Thermal conductivity at high temperatures (300–900 K) was calculated using $\kappa = C_v d \rho_D$, where d is the thermal diffusivity measured, using NETZCH Laser Flash system (LFA 457), ρ_D is the mass density of the samples, and $C_v \approx C_p$ is specific heat capacity at constant pressure measured using NETZCH high temperature differential scanning calorimetry (DSC) system (Pegasus 404). There was very good agreement between the low and high temperature measurements of both electronic and thermal transport properties as can be observed in Figures 2 and 4. The carrier concentration is determined as a function of temperature from 10–300 K by Hall coefficient measurements using the commercial Quantum Design Physical Properties Measurement System (PPMS) under low (± 0.5 T) and high (± 3 T) magnetic fields, which showed no change in the carrier concentration, n . Elastic moduli were measured using resonant ultrasound spectroscopy (RUS)³² from 300–750 K at the National Center for Physical Acoustics at the University of Mississippi. Experimental details for high temperature RUS measurements can be found in the following Ref. 33.

III. RESULTS AND DISCUSSION

A. XRD and microstructure

The crystal structure and phase purity of densely packed, $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_{3-\delta}$ ($x=0.05$ to 0.1) ceramics have been confirmed by XRD patterns, as shown in Figure 1(a). Quantitative analysis using Rietveld refinement indicates that a cubic SrTiO_3 phase with a space group $Pm\bar{3}m$ [JCPDS card #01-086-0177] constitutes about $\sim 99\%$ of the total weight, with reflections of minute amounts of Y_2O_3 [JCPDS card #01-074-1828]. The goodness of fit obtained for all the compositions range from $S \sim 1.5$ to 2.0 with R_{wp} values ranging from 14% – 18% . A shift in diffraction peaks is observed at higher angles with Y-doping from $x=0$ to $x=0.1$, indicating that the lattice is shrinking with incorporation of Y at Sr-site. The lattice parameters estimated using Rietveld refinement are in good agreement with reported values.

The micro-structural analysis of $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_{3-\delta}$ series using SEM indicates close-packed grains with no observable porosity, contrary to previous reports of porous microstructure in the Y-doped SrTiO_3 .²³ Figure 1(b) shows the SEM image of a polished sample surface of $x=0.075$. The

FIG. 1. (a) High Resolution X-ray Diffraction patterns of $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_{3-\delta}$, $x=0.05, 0.075, 0.1$ (b) SEM image of a polished surface of $x=0.075$.

observed grains are close-packed with distinct grain boundary and average grain size ~ 5 – $10 \mu\text{m}$.

B. Electronic transport

Figure 2(a) shows the temperature dependence of electrical resistivity in the $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_{3-\delta}$ series from $(10$ – $750)$ K. Electrical resistivity shows degenerate semiconducting or “metal-like” behavior, increasing linearly with increasing temperature above 400 K. The residual resistivity of the doped samples decreases with increasing Y content from $x=0.05$ to 0.1 , with $x=0.1$ exhibiting the lowest residual resistivity in the series. At room temperature, the electrical resistivity (ρ) drops from $\rho \sim 4 \text{ m}\Omega\text{-cm}$ in $x=0.05$ to $\rho \sim 0.8 \text{ m}\Omega\text{-cm}$ ($\sigma \sim 1250 \text{ S/cm}$) in $x=0.1$. Hall coefficient measurements indicate a high value of the carrier concentration (n) of $3 \times 10^{20} \text{ cm}^{-3}$ in $x=0.05$ increasing to $\sim 2 \pm 0.5 \times 10^{21}$ in the $x=0.1$. To the best of our knowledge, there are no previous reports of carrier concentration in the Y-doped SrTiO_3 ceramics in the literature. The Hall mobility ($\mu = 1/ne\rho$) decreases with increasing Y-doping from $x=0.05$ to 0.1 at

FIG. 2. (a) Electrical resistivity as a function of temperature, and (b) temperature dependence of electron mobility of $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_{3-\delta}$, $x=0.05, 0.1$.

room temperature as shown in Figure 2(b). In the $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$ ceramic, electron mobility ($\mu = 1/ne\rho$) is estimated to be low with $\mu \sim 9 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$ at 15 K, which decreases to $\sim 4 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$ at 300 K. The electron mobility in the $\text{Sr}_{0.95}\text{Y}_{0.05}\text{TiO}_{3-\delta}$ varies from $\sim 15 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$ at 15 K, which reduces to $\sim 7 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$ at 300 K. With n found to be temperature independent, both the electrical conductivity and the mobility decrease as a function of temperature as $T^{-0.8}$ and $T^{-0.9}$ in $x = 0.05$ and 0.1 , respectively, in the temperature range of 150–300 K indicating a possible mixed scattering phenomenon in this temperature range. Other groups have reported a change in the dominant scattering mechanism at $T \sim 750 \text{ K}$ in La-doped SrTiO_3 , with mobility varying as $T^{-2.0}$ below 750 K, indicating mixed acoustic and polar optical phonon scattering occurring, and as $T^{-1.5}$ above 750 K indicating only acoustic phonon scattering above 750 K.³⁴

Figure 3(a) shows the temperature dependence of thermopower or Seebeck coefficient as a function of temperature from (10–800) K in the above series. The thermopower in this series exhibit high values ranging from $\alpha \sim -330 \mu\text{V/K}$

in $x = 0.05$ and $\alpha \sim -200 \mu\text{V/K}$ in $x = 0.1$ at 760 K. The materials show n-type behavior that is diffusive in nature, increasing linearly with temperature up to about 425 K. Above 425 K, the slope of thermopower changes slightly with increase in temperature, due to possible changes in scattering mechanisms. The change in slope above 425 K is clearly evident in the $d\alpha/dT$ behavior of $x = 0.075$ and 0.1 , as shown in the inset of figure 3(a). Similar anomalies in the thermopower were observed by other groups³⁵ at higher temperatures $\sim 750 \text{ K}$. Ohta *et al.*³⁴ showed the temperature dependence of the calculated carrier scattering parameter r in La and Nb-doped SrTiO_3 single crystals and found it to decrease from $r = 0.5$ to $r = 0$ at $\sim 750 \text{ K}$, indicating both polar optical and acoustic phonon scattering below 750 K and acoustic phonon scattering above 750 K. Using a simple parabolic band approximation, the effective masses of $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_{3-\delta}$ series are calculated from measured thermopowers and carrier concentration (n) at room temperature using the relation³⁶

$$\alpha = \left(\frac{8\pi^2 k_B^2}{3eh^2} \right) m^* T \left(\frac{\pi}{3n} \right)^{2/3} (1+r), \quad (2)$$

where the scattering parameter r determines the energy-dependence of the relaxation time in the power law form, $\tau(E) = \tau_0 E^{r-1/2}$. With $r = 0.5$ corresponding to polar optical phonon scattering, the effective masses of $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_{3-\delta}$ are estimated from thermopower (α) vs. carrier concentration (n) at room temperature in the Pisarenko plot shown in Figure 3(b). It is observed that the value of the effective masses in the $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_{3-\delta}$ ($x = 0.05, 0.075, 0.1$) is about $m^* \sim 3.5 m_e$. Effective mass of $(6.0\text{--}6.6)m_e$ have been reported in the La-doped SrTiO_3 by Ohta *et al.*³⁴

The combination of high thermopowers $\alpha > -80 \mu\text{V/K}$ and moderately low electrical resistivity values, $\rho < 5 \text{ m}\Omega\text{-cm}$ at a carrier concentration, $n \sim 10^{21} \text{ /cm}^3$ at 300 K in the $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$ strongly suggest degenerate semiconducting behavior. The thermoelectric power factors increase with increased Y-doping, giving rise to a high values of power factor, $\text{PF} \sim \alpha^2 \sigma T \sim 0.84 \text{ W/m-K}$ at 750 K, in the $x = 0.1$.

C. Thermal transport and thermoelectric figure-of-merit

Figure 4(a) shows the total thermal conductivity (κ) of $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$ compared to pure $\text{SrTiO}_{3-\delta}$ in the temperature range of (10–900) K. The temperature dependence of measured κ_T matches well with that of single crystalline $\text{SrTiO}_{3-\delta}$ measured by Muta *et al.*²² at $T > 300 \text{ K}$. As seen in Figure 4(a), pure $\text{SrTiO}_{3-\delta}$ exhibits a broad peak in κ_T at $T_p \sim 150 \text{ K}$, which is suppressed considerably by Y-doping, due to increased phonon scattering by point defects. The thermal conductivity is observed to increase slowly with temperature, which may be attributed to the high Debye temperature ($\sim 513 \text{ K}$) reported in these materials.³⁷ The κ_T of $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$ is further reduced to about $\sim 2.7 \text{ W/m-K}$ at 760 K compared to $\sim 3.6 \text{ W/m-K}$ in $\text{SrTiO}_{3-\delta}$ at the same temperature. The electronic transport properties of $\text{SrTiO}_{3-\delta}$ will be presented in details elsewhere.³⁸ Combining the high

FIG. 3. (a) Seebeck coefficient of $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_{3-\delta}$ $x = 0.05, 0.075$, and 0.1 . Inset shows $-(d\alpha/dT)$, indicating a change in slope in thermopower above 400 K, shown by arrows. (b) Pisarenko plot.

FIG. 4. (a) Total thermal conductivity of $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_3$ ($x=0.0, 0.1$), compared with single crystalline SrTiO_3 by Muta *et al.*²² and minimum thermal conductivity estimated using Cahill's model. (b) Thermoelectric figure of merit, ZT, of $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_3$ compared to other groups.³⁹

TE power factor, $\text{PF} \sim 0.84 \text{ W/m-K}$ and the comparatively low thermal conductivity in the $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_3$, a $\text{ZT} \sim 0.3$ at 760 K is achieved, which is the highest ZT value reported thus far in the Y-doped SrTiO_3 ceramics³⁹ (Figure 4(b)). A $\text{ZT} \sim 0.35$ at $T \sim 1000 \text{ K}$ is the highest ZT reported in the polycrystalline $\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3$ ceramic oxide, which is at a much higher temperature of operation compared to our current results.⁴⁰

Based on a phenomenological model proposed by Cahill *et al.*,^{41,42} we estimate the minimum thermal conductivity using

$$\kappa_{\min} = \left(\frac{\pi}{6}\right)^{1/3} k_B n_a^{2/3} \sum_i v_i \left(\frac{T}{\theta_i}\right)^2 \int_0^{\theta_i/T} \frac{x^3 e^x}{(e^x - 1)^2} dx, \quad (3)$$

where n_a is the number of atoms per unit volume, v_i is the sound velocity, and θ_i is the cut-off frequency in the unit of K for polarization mode i . Using the room temperature value of

the mean velocity of sound of pure $\text{SrTiO}_{3-\delta}$ estimated from RUS measurements discussed in Sec. E, we estimate a cut-off frequency, $\theta_i = v_i (\hbar/k_B) (6\pi^2 n_a)^{1/3} \sim 674 \text{ K}$. Substituting the value of θ_i in the above equation, a $\kappa_{\min}$ in the temperature range of 10–1000 K is estimated as shown in the Figure 4(a). Our estimated value of $\kappa_{\min} \sim 1.5 \text{ W/m-K}$ at room temperature and 1.8 W/m-K at 1000 K in SrTiO_3 are in fair agreement with $\kappa_{\min} \sim 1.4 \text{ W/m-K}$ at 300 K and $\sim 1.8 \text{ W/m-K}$ at 1000 K reported by Wang *et al.*⁴³ Our calculation of $\kappa_{\min}$ is applied to SiO_2 and $\text{Zr}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$ reported in Cahill's paper in the temperature range 10–300 K for comparison and it is in good agreement with the reported values.⁴¹

As observed in Figure 4(a), the κ_T of the $\text{SrTiO}_{3-\delta}$ measured at room temperature is higher, almost by a factor of 2 compared to the theoretical minimum estimated using Cahill's model. Hence phonon scattering mechanisms via Y-doping on the lattice thermal conductivity (κ_L) are investigated using a phenomenological Callaway's model. With 10% Y-doping at the Sr site in $\text{SrTiO}_{3-\delta}$, κ_L decreases considerably via increased phonon scattering due to elastic strain field effects, as discussed in the later sections.

D. Modified Callaway's model

The electronic contribution to thermal conductivity (κ_E) is estimated by the Wiedemann Franz relation: $\kappa_E = L_0 \sigma T$, where the Lorentz number, $L_0 = 2.0 \times 10^{-8} \text{ V}^2/\text{K}^2$ for a degenerate semiconductor.⁴⁴ The lattice thermal conductivity (κ_L) is estimated by subtracting the electronic part from the total thermal conductivity, κ_T . The temperature dependence of κ_L is a signature behavior resulting from different phonon scattering mechanisms that limit thermal conduction at low and high temperatures as discussed below. In the Debye model using relaxation time approximation, a phenomenological model for κ_L is given by Callaway^{45,46} as represented by

$$\kappa_L(x) = \frac{k_B}{2\pi^2 v_s} \left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^4 e^x}{\tau_{ph}^{-1} (e^x - 1)^2} dx, \quad (4)$$

where $x = \hbar\omega/k_B T$ is the reduced phonon frequency, ω is the phonon frequency, $\hbar$ is the reduced Planck constant, k_B is the Boltzmann constant, and T is the absolute temperature. The total relaxation time (τ_{ph}) is given by $\tau_{ph}^{-1} = \tau_{PD}^{-1} + \tau_U^{-1} + \tau_B^{-1}$, consisting of phonon scattering by point defects ($\tau_{PD}^{-1} = A\omega^4$), the anharmonic phonon-phonon or Umklapp (U) scattering ($\tau_U^{-1} = B\omega^2 T e^{-\theta_D/3T}$), and the phonon-boundary scattering ($\tau_B^{-1} = v_s/D$), respectively. Callaway's model assumes that the phonon scattering effects are additive following Matthiessen's rule^{47,48} and all the scattering processes, except boundary scattering can be represented by frequency-dependent relaxation times. The model assumes that heat is carried by acoustic phonons and makes no distinction between longitudinal and transverse phonons. A single averaged phonon velocity approximately equal to the velocity of sound v_s is assumed over the entire temperature range. For boundary scattering, D represents an effective phonon mean

free path, limited by average grain size (polycrystals) or crystal geometry (single crystals).⁴⁹ The relaxation time for point defect scattering (τ_{PD}) estimated by Klemens^{50,51} is given by

$$\tau_{PD}^{-1} = A\omega^4 = \frac{V}{4\pi v_s^3} \omega^4 \Gamma, \quad (5)$$

which is similar to Rayleigh scattering of phonons and represents a combination of impurity and isotope scattering, where the point defect scattering parameter related to mass fluctuation scattering is Γ , V is the volume per atom, and v_s is the phonon velocity. The point defect term is modified by Abeles⁵² to include the effects of strain field scattering as follows:

$$\Gamma = \Gamma_{MF} + \Gamma_{SF} = \sum_i x_i \left[\left(\frac{\Delta M_i}{M} \right)^2 + \varepsilon \left(\frac{\Delta \delta_i}{\delta} \right)^2 \right], \quad (6)$$

where Γ_{MF} and Γ_{SF} represent the point defect scattering parameters arising from mass fluctuation scattering and strain field scattering effects, respectively, ΔM is the mass difference of the host and the impurity atom, M is the mass of the average ternary cluster, ε is a phenomenological strain parameter, $(\Delta \delta_i)$ is the difference in ionic radii of the host and the impurity atom, and δ is the average ionic radii.^{53,54} The relaxation time for three-phonon Umklapp process in Callaway's model is given by $\tau_U^{-1} = B_1 \omega^2 T^3$, where B_1 contains an exponential temperature factor $\sim e^{-\theta_D/AT}$. The effect of the normal phonon scattering process, which is valid for low frequency longitudinal phonons and makes no direct contribution to the thermal resistance, has been neglected.^{55–57} Currently, the relaxation time for Umklapp scattering proposed by Slack *et al.*⁵⁸ based on a model by Leibfried and Schlomann⁵⁹ is used as follows:

$$\tau_U^{-1} = B\omega^2 T e^{-\theta_D/3T} \approx \frac{\hbar \gamma^2}{M v_s^2 \theta_D} \omega^2 T e^{-\theta_D/3T}, \quad (7)$$

where θ_D is the Debye temperature, M is the average mass of an atom in the crystal, and γ is the Grüneisen parameter. Using the modified Callaway's equation (Eq. (4)), the lattice thermal conductivities of $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_3$ ($x=0.05, 0.1$) are modeled in the temperature range (30–600) K as shown in Figure 5. Assuming mass fluctuation and strain field scattering effects occurring between the Sr and Y atoms only, the point defect scattering parameter $A(\text{calc})$ from Eqs. (5) and (6) and the Umklapp scattering parameter $B(\text{calc})$ from Eq. (7) are theoretically calculated using measured and reported material parameters as discussed below. The values of $A(\text{calc})$ and $B(\text{calc})$ are used as initial guesses for fitting the experimental results as listed in Table I. The actual fitting parameters $A(\text{fit})$ and $B(\text{fit})$ are also tabulated for comparison. The Umklapp scattering and point defect scattering fitting parameters A and B are observed to be within similar orders of magnitude as estimated in other materials.⁶⁰

In addition, above 350 K, a modification suggested by Slack *et al.*⁶¹ is used to model κ_L as follows:

FIG. 5. Lattice thermal conductivity of $x=0.05$ and 0.1 modeled using modified Callaway's equation. The vertical dotted line near 360 K separates the fits at low (LT) and high temperatures (HT).

$$\kappa_L = \frac{k_B}{2\pi^2 v_s} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{\theta_D/T} \tau_c x^2 dx \quad (8)$$

with $\tau_c^{-1} = (B_U T + B_H T^2) \omega^2 + A \omega^4$, where A is the relaxation time for point defect scattering as defined in Eq. (5), B_U and B_H are relaxation times for Umklapp scattering, with B_H a higher order four-phonon scattering parameter. The parameters $A(\text{HT})$, B_U , and B_H used for fitting data at high temperatures are listed in Table I. While the calculated parameter, $A(\text{calc})$ is the same over the entire temperature range, the

TABLE I. Fitting parameters used in Callaway's model, where Γ_{MF} and Γ_{SF} are the point defect scattering parameters due to mass fluctuation scattering and elastic strain field effect respectively, ε is a phenomenological strain parameter, A and B are point defect and Umklapp scattering parameters, B_U and B_H are the high temperature Umklapp fitting parameters, v_s is the mean velocity of sound, D is the average grain diameter, x is a correction factor, Θ_D is the Debye temperature, and γ is the Grüneisen parameter.

X	0.0	0.05	0.1	References
$\Gamma_{MF}(\text{calc})$	...	6×10^{-5}	1×10^{-4}	
$\Gamma_{SF}(\text{calc})$	...	5×10^{-2}	1×10^{-1}	
ε	...	39 §	39	§[52]
$A(\text{calc}) (\text{s}^3)$	...	4×10^{-43}	8×10^{-43}	
$A(\text{fitted}) (\text{s}^3) (\text{LT})$	...	2.8×10^{-43}	5.0×10^{-43}	
$A(\text{fitted}) (\text{s}^3) (\text{HT})$	...	3.0×10^{-43}	9.7×10^{-43}	
$B(\text{calc}) (\text{sK}^{-1})$	...	5×10^{-19}	5×10^{-19}	
$B(\text{fitted}) (\text{sK}^{-1})$	...	9.4×10^{-18}	9.0×10^{-18}	
$B_U(\text{fitted})$	...	4.9×10^{-18}	4.9×10^{-18}	
$B_H(\text{fitted})$	...	0.001×10^{-21}	0.001×10^{-21}	
v_s at 300 K (ms^{-1})	5172	5040	4908	
$D (\mu\text{m})$	...	5	5	
$v_s x D (\text{fit}) (\text{s}^{-1})$	...	3.4×10^{11}	4.0×10^{11}	
X	...	0.003	0.002	
$\Theta_D (\text{K})$	513 *	500	490	* [37]
γ	1.5 ♦	1.6	1.7	♦[66]

parameters $A(\text{fitted})(\text{HT})$ and $A(\text{fitted})(\text{LT})$ denote the point defect scattering parameters used for fitting κ_L at high (HT) and low temperatures (LT), respectively. The small variation between $A(\text{fitted})(\text{HT})$ and $A(\text{fitted})(\text{LT})$ possibly arise from the different Umklapp scattering parameters used above and below 360 K. As observed from Figure 5, the model can account for the experimental data within $<\pm 2.5\%$, up to a temperature of about 400 K, above which other phonon scattering mechanisms might become prominent and need to be accounted for.

Some of the approximations used in the model are discussed below, which may explain the uncertainties observed between calculated and fitted parameters. The mean velocities of sound v_s of pure $\text{SrTiO}_{3-\delta}$ and $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$ in the temperature range 300–800 K are estimated from elastic moduli measured using resonant ultrasound spectroscopy discussed in Sec. E. The average v_s at 300 K is extrapolated for $x = 0.05$ from a linear fit between $x = 0.0$ and 0.1 , which is listed in Table I. In addition, the elastic moduli of pure $\text{SrTiO}_{3-\delta}$ is known to undergo a lattice softening at the SPT at 105 K due to rotation of the TiO_6 octahedra,^{12,62} which makes the low temperature dependence and value of v_s unknown in both pure and doped $\text{SrTiO}_{3-\delta}$. Moreover, it is observed that in materials with an Umklapp peak at higher temperatures, $T_p > 150$ K, it is usually difficult to model the temperature dependence of κ_L below the peak using an inverse relaxation time of v_s/D . This is possibly due to the increased phonon interactions between the grain-boundary scattered phonons at these higher temperatures,⁶³ leading to a phonon mean free path that is smaller than the size of the grain, D . As observed from Figure 3(a), the Umklapp peak in pure and doped SrTiO_3 ceramics are at a high temperature $T_p \sim 150$ K. Assuming boundary scattering to be a semi-diffusive scattering mechanism at these temperatures, a correction factor, $x^{64,65}$ is used to model the temperature dependence of κ_L and the value of v_s/xD , indicating is listed in Table I. The Debye temperature θ_D of the doped ceramics are arbitrarily fixed at values lower than $\theta_D \sim 513$ K reported for pure $\text{SrTiO}_{3-\delta}$ as listed in Table I. The Grüneisen parameter for pure SrTiO_3 is reported to be $\gamma = 1.5$.⁶⁶ The Grüneisen parameter, which is a measure of the anharmonicity of the crystal lattice, would be higher in the Y-doped SrTiO_3 , and they have been arbitrarily set at higher values as shown in Table I. The uncertainty between $B(\text{calc})$ and $B(\text{fit})$ is slightly higher, which could be originating from the uncertainty in the parameters used to estimate $B(\text{calc})$.

Nevertheless, the point defect scattering parameter A , which is comprised of both mass fluctuation scattering (Γ_{MF}) and strain field scattering (Γ_{SF}), increases with increasing Y-doping as observed from Table I. The atomic masses of Sr (87.6 g/mol) and Y (88.9 g/mol) are similar due to their close proximity in the periodic table, but the ionic radii of Y^{3+} (~ 1.23 Å, coordination number 12) is smaller than Sr^{2+} (~ 1.44 Å, coordination number 12) ions. In a non-ideal crystal structure, ions and atoms of different ionic radii may scatter phonons due to localized distortion of their bond lengths, thus forming elastic strain fields in the lattice.⁶⁷ It is observed that $\Gamma_{\text{MF}} \ll \Gamma_{\text{SF}}$ and the increase in A occurs chiefly from an increase in Γ_{SF} . The reduction of κ_L thus

arises from scattering of phonons by elastic strain fields in the lattice due to the smaller ionic radii of Y^{3+} with respect to Sr^{2+} ions.

E. Elastic moduli and mean velocity of sound

The effect of Y-doping on the elastic moduli of SrTiO_3 lattice is further investigated using *RUS* in the temperature range 300–750 K. Small grained polycrystalline materials are elastically isotropic and thus exhibit only two independent elastic moduli, a longitudinal modulus c_{11} , and the shear modulus c_{44} , which are related to the longitudinal and transverse velocities of sound respectively. Figures 6(a) and 6(b) show the two elastic moduli as a function of temperature for polycrystalline $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_{3-\delta}$ ($x = 0, 0.1$) ceramics. As the temperature increases from 300 to 750 K, both c_{11} and c_{44} of pure $\text{SrTiO}_{3-\delta}$ are found to decrease, as is typical for solids.⁶⁸ In contrast, the temperature dependence of elastic moduli of $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$ shows a distinct anomaly, where the c_{44} remains almost unchanged in between 300–600 K and then gradually decreases with increasing temperature.

FIG. 6. Elastic moduli (a) c_{11} and (b) c_{44} , vs. temperature of $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_3$ ($x = 0.0, 0.1$). A distinct anomaly is observed in $x = 0.1$.

The internal friction, $Q^{-1} = \Delta f/f$ (where Q is the quality factor of resonance estimated from the half-width at full maximum (FWHM) of the resonant frequencies and f refers to the center frequency of the resonance peak), shows a similar anomaly over the temperature range 300–600 K. The mean velocity of sound, v_s , is estimated in the pure and $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$ from 300 to 750 K with the measured values of c_{11} and c_{44} .^{69,70}

$$v_s = \left(\frac{1}{3} \left[\frac{2}{v_T^3} + \frac{1}{v_L^3} \right] \right)^{-1/3}, \quad (9)$$

where $v_L = \sqrt{\frac{c_{11}}{\rho}}$ and $v_T = \sqrt{\frac{c_{44}}{\rho}}$ are the longitudinal and transverse velocities of sound as shown in Figure 7(a). The anomaly is also observed in the temperature dependence of v_s in the $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$ ceramic. Our measurements of longitudinal and transverse velocities of $\text{SrTiO}_{3-\delta}$ are in good agreement with other groups.^{22,71} The value of v_s in $x = 0.0$ ranges from 5172 m/s to 4932 m/s at 300 K and 723 K, respectively. The velocity of sound is lower in the

$\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$ ranging from 4908 m/s to 4855 m/s at 300 K and 723 K, respectively. As observed in Figure 3(a), the slope of the thermopower changes at ~ 425 K in the $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$, possibly due to change in phonon scattering mechanisms. Although no anomaly in the elastic moduli is observed in $x = 0.0$, a similar change of slope is observed in the thermopower of pure $\text{SrTiO}_{3-\delta}$ at this temperature (results presented elsewhere).³⁸ Hence, a direct correlation between the anomaly in elastic moduli in $x = 0.1$ and the change in slope of the thermopower could not be made. Although the exact nature of the anomaly in the elastic moduli of $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$ needs to be further investigated, it is possible that at higher temperatures, the elastic strain generated in the lattice due to smaller ionic radii of Y with respect to Sr is observed in the elastic moduli behavior.

F. Phonon mean free path

The anomaly in the elastic moduli of $x = 0.1$ further reflects increased phonon scattering in the $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$. Using the mean velocity of sound (or the phonon velocity) estimated from RUS measurements in $x = 0.0$ and 0.1 in the temperature range 300–800 K, the phonon mean free paths (ℓ) of $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_{3-\delta}$ ($x = 0.0$ and 0.1) are calculated using the relation from the kinetic theory of gases, $\kappa_L = 1/3 c_v v_s \ell$, where κ_L is the lattice thermal conductivity, c_v is the specific heat per unit volume of phonons, and v_s is the phonon velocity which is the mean velocity of sound. Figure 7(b) shows the phonon mean free paths of $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$ and $\text{SrTiO}_{3-\delta}$, estimated using measured values of heat capacity, velocities of sound and κ_L values obtained from measured thermal conductivity in this temperature range. As observed from the figure, the value of ℓ is comparatively lower in $x = 0.1$, compared to the pure $\text{SrTiO}_{3-\delta}$, which signifies that Y-doping is effective in increasing phonon scattering in these oxides. The low values of $\ell < 2$ nm in the $\text{SrTiO}_{3-\delta}$ are comparable to the values reported by Wang *et al.*⁴³ These low values of ℓ also indicate that nano-structuring may not be an effective option for reducing κ_L in the SrTiO_3 oxides.

IV. CONCLUSIONS

The effect of Y-doping on the thermoelectric properties of $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_{3-\delta}$ ($x = 0.05, 0.075, 0.1$) ceramics are systematically investigated from (15–800) K, respectively. The doped samples indicate degenerate semiconducting behavior, simultaneously exhibiting high thermopower ($\alpha \sim -200$ $\mu\text{V/K}$) and moderate electrical conductivity ($\sigma \sim 250$ S/cm) in the $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$ ceramic, which gives rise to a high thermoelectric power factor defined herein as $(\alpha^2 \sigma T) \sim 0.84$ W/m-K at $T \sim 760$ K. The lattice thermal conductivities are suppressed with increased Y-doping due to strain field scattering effect owing to the smaller ionic radii of Y with respect to Sr ions. A comparatively low $\kappa_T \sim 2.7$ W/m-K at 760 K in the $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$ yields the largest ZT ~ 0.3 at 760 K reported to date in the Y-doped SrTiO_3 ceramics. A modified Callaway's equation is used to model the temperature dependence of the lattice thermal conductivity from 10–600 K, which confirms the effect of strain field scattering in reducing the lattice thermal

FIG. 7. (a) Mean velocity of sound, and (b) Phonon mean free path vs. temperature of $\text{Sr}_{1-x}\text{Y}_x\text{TiO}_3$ ($x = 0.0, 0.1$).

conductivity in the series. The correlation between the coefficients of the point defect scattering parameter A (estimated from mass fluctuation and strain field scattering) obtained with experimental fits and theoretical model shows a systematic relationship between ceramic composition and the lattice thermal conductivity. Additionally, an anomaly in the elastic moduli and the mean velocity of sound are observed in the $\text{Sr}_{0.9}\text{Y}_{0.1}\text{TiO}_{3-\delta}$ in contrast to $\text{SrTiO}_{3-\delta}$, further indicating increased phonon scattering due to Y-doping.

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