New insights on the synthesis and electronic transport in bulk polycrystalline Pr-doped SrTiO₃- δ

Arash Mehdizadeh Dehkordi, Sriparna Bhattacharya, Taghi Darroudi, Husam N. Alshareef, and Terry M. Tritt

Citation: *Journal of Applied Physics* **117**, 055102 (2015); doi: 10.1063/1.4905417

View online: <http://dx.doi.org/10.1063/1.4905417>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/117/5?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Role of phonon scattering by elastic strain field in thermoelectric Sr_{1-x}Y_xTiO₃- \$\delta\$](#)

J. Appl. Phys. **115**, 223712 (2014); 10.1063/1.4882377

[Influence of rare earth doping on thermoelectric properties of SrTiO₃ ceramics](#)

J. Appl. Phys. **114**, 223714 (2013); 10.1063/1.4847455

[Transport and thermoelectric properties of Sr₃\(Ti_{0.95}R_{0.05}\)₂O₇ \(R=Ta, Nb, W\) oxides](#)

J. Appl. Phys. **112**, 124904 (2012); 10.1063/1.4769787

[Effect of Pr substitution on structural and dielectric properties of SrTiO₃](#)

J. Appl. Phys. **112**, 044106 (2012); 10.1063/1.4747937

[Nb-doped SrTiO₃ glass-ceramics as high temperature stable n-type oxide thermoelectrics](#)

AIP Conf. Proc. **1449**, 343 (2012); 10.1063/1.4731567

The logo for the Journal of Applied Physics, featuring the letters 'AIP' in a large, bold, white font on an orange background, followed by the text 'Journal of Applied Physics' in a smaller, white font.

Meet The New Deputy Editors

Christian
Brosseau

Laurie
McNeil

Simon
Phillpot

New insights on the synthesis and electronic transport in bulk polycrystalline Pr-doped $\text{SrTiO}_{3-\delta}$

Arash Mehdizadeh Dehkordi,^{1,a)} Sriparna Bhattacharya,² Taghi Darroudi,³ Husam N. Alshareef,⁴ and Terry M. Tritt^{1,2,b)}

¹*Department of Materials Science and Engineering, Clemson University, Clemson, South Carolina 29634, USA*

²*Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29634, USA*

³*Electron Microscope Facility, Clemson Research Park, Clemson University, Clemson, South Carolina 29634, USA*

⁴*Materials Science and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 29634, Saudi Arabia*

(Received 5 October 2014; accepted 21 December 2014; published online 2 February 2015)

Recently, we have reported a significant enhancement in the electronic and thermoelectric properties of bulk polycrystalline SrTiO_3 ceramics via praseodymium doping. This improvement was originated from the simultaneous enhancement in the thermoelectric power factor and reduction in thermal conductivity, which was contributed to the non-uniform distribution of Pr dopants. In order to further understand the underlying mechanism, we herein investigate the role of praseodymium doping source (Pr_2O_3 versus Pr_6O_{11}) on the synthesis and electronic transport in Pr-doped SrTiO_3 ceramics. It was observed that the high-temperature electronic transport properties are independent of the choice of praseodymium doping source for samples prepared following our synthesis strategy. Theoretical calculations were also performed in order to estimate the maximum achievable power factor and the corresponding optimal carrier concentration. The result suggests the possibility of further improvement of the power factor. This study should shed some light on the superior electronic transport in bulk polycrystalline Pr-doped SrTiO_3 ceramics and provide new insight on further improvement of the thermoelectric power factor. © 2015 AIP Publishing LLC.

[<http://dx.doi.org/10.1063/1.4905417>]

I. INTRODUCTION

SrTiO_3 (STO) is a large band gap insulator exhibiting intriguing properties ranging from superconductivity,¹ ferroelectricity,² photoluminescence,³ and recently thermoelectricity.⁴ The majority of these phenomena were induced (observed) by modification of the perovskite lattice via either creation of oxygen vacancies and/or substitutional doping. Among the variety of dopants used to dope the “STO” lattice, praseodymium-doped STO displayed unique properties such as room-temperature ferroelectricity,⁵ colossal dielectric constant,⁶ photoluminescence,^{7,8} and thermoelectric properties (specifically, a very large thermoelectric power factor).^{9,10} The thermoelectric power factor, PF, is a measure of the potential of the electronic transport in a material for thermoelectric applications and is defined herein as $PF = \alpha^2 \sigma T$, where α is the Seebeck coefficient, σ the electrical conductivity, and T the absolute temperature in Kelvin.

Recently, we have reported a large thermoelectric power factor of $\sim 1.3 \text{ W m}^{-1} \text{ K}^{-1}$ at 500°C (773 K) for bulk polycrystalline Pr-doped SrTiO_3 , which is the largest ever reported for any doped single- or poly-crystalline SrTiO_3 .^{9,10} Such a significant improvement has not been reported for any other dopants.^{11–13} It was experimentally concluded that the enhancement was originated from the non-uniform distribution of Pr dopants. However, further investigation is still

required in order to fully understand the underlying mechanism. One of the possible explanations that need to be investigated is the role of multivalent nature of Pr on the electronic transport in Pr-doped SrTiO_3 . Of the three lanthanides (Ce, Pr, and Tb), which are well-known to exist in a trivalent as well as tetravalent state in binary oxides, only Pr has been studied as an Sr-site dopant for thermoelectric applications. To the best of our knowledge, all the previous reports on doping SrTiO_3 with Pr have employed Pr_6O_{11} (Pr^{3+} and Pr^{4+}) as the Pr doping source. However, Pr_2O_3 (predominantly Pr^{3+}) was used as the Pr doping source in our previous reports on ceramics possessing a large thermoelectric power factor. Therefore, we were intrigued to systematically investigate this observation.

In this paper, in an attempt to further understand the reported superior electronic transport in $\text{Sr}_{1-x}\text{Pr}_x\text{TiO}_3$ ceramics, we investigate a comparative study on the role of praseodymium doping source on the electronic transport in these ceramics. Furthermore, theoretical calculations were performed based on Boltzmann transport theory in order to estimate the maximum achievable power factor and the corresponding optimal doping concentration. These results provide new insight to further improve the thermoelectric power factor in these oxides.

II. EXPERIMENTAL DETAILS

Two typical batches of $\text{Sr}_{1-x}\text{Pr}_x\text{TiO}_3$ powder with $x = 0.075$ were prepared via solid-state reaction route from

^{a)}amehdiz@g.clemson.edu

^{b)}tritt@clemson.edu

different praseodymium oxides as the source of doping. Stoichiometric amounts of SrCO_3 powder (99.9%; Aldrich), TiO_2 nanopowder (99.5%; Aldrich), and Pr_2O_3 sintered lumps (99.9%; Alfa Aesar) for the first batch, and Pr_6O_{11} powder (99.9%; Alfa Aesar) for the second batch were ground, mixed, cold pressed into pellets and then calcined in air at 1400°C with intermediate grinding according to the following reactions:

The calcined pellets were subsequently ground into powders using a mortar and pestle. The resulting powders were densified into disks (12.7 mm in diameter and 3 mm thick) using spark plasma sintering (SPS) technique (Dr. Sinter Lab, SPS-515S) under dynamic vacuum at $1400\text{--}1500^\circ\text{C}$ for 5 min. Similar SPS conditions (load, heating/cooling rate, and pulse ratio) were employed for both samples. Densities, ρ , of the bulk samples were determined using the Archimedes method and are all higher than 95% of their theoretical values. Rectangular bars ($10 \times 2 \times 2 \text{ mm}^3$) were cut from the disks for the measurements of electrical conductivity (σ) and Seebeck coefficient (α). These measurements were performed using an Ulvac-Riko ZEM-3 (300 K to 800 K) system. Uncertainties in the measurements of electrical conductivity and Seebeck coefficient are $\pm 3\%$ and $\pm 2\%$, respectively. Carrier concentration of the samples was determined with a Quantum Design PPMS system using five-probe configuration under low (0.5 T) and high (3 T) magnetic fields (10 K to 300 K). All the transport measurements reported for a given composition were performed on the same sample. Structure and microstructure of the powders as well as the bulk samples were studied using a Rigaku Ultima IV high resolution X-ray diffraction (XRD) with Cu $K\alpha$ doublet radiation and a Hitachi SU-6600 field emission scanning electron microscope (FESEM). Energy dispersive X-ray spectroscopy (EDS, Oxford Instruments) was also performed to investigate the chemical composition of the specimens.

III. RESULTS AND DISCUSSIONS

XRD patterns of the raw Pr_2O_3 and Pr_6O_{11} powders used as the doping source as well as the corresponding simulated powder diffraction patterns, obtained with the PowderCell software package,¹⁴ are shown in Figure 1. Diffraction pattern of the Pr_2O_3 powder (light green in color) can be readily indexed to the Pr_2O_3 trigonal lattice (space group $P\bar{3}m1$), while that of the Pr_6O_{11} (dark brown-black in color) can be indexed to a tetragonal cell (space group $P2_1/c$), which are shown in Figure 2. It is observed that a small amount of a secondary phase is present in both powders (shown with ■ and ▲ in Fig. 1). These reflections could not be identified from the ICDD powder diffraction database (PDF). However, they might be associated to the distorted

FIG. 1. X-ray diffraction (XRD) profiles of fresh Pr_2O_3 and Pr_6O_{11} powders, and the corresponding simulated diffraction patterns using PowderCell. ■ and ▲ show the reflections attributed to secondary phase(s).

lattice of the intermediate phases (such as Pr_5O_9 or PrO_2) in the Pr-O phase diagram.

Diffraction profiles of Pr-doped SrTiO_3 powders prepared from Pr_2O_3 and Pr_6O_{11} doping sources, respectively, are compared in Figure 3(a). Formation of SrTiO_3 phase is confirmed in both powders and the reflections can be indexed to a cubic lattice with $Pm\bar{3}m$ space group and a lattice parameter of $a = 3.906 \text{ \AA}$. Two extra reflections (shown with ▼ in Figure 3(a)) with weak intensities were also observed similarly in both powders, which correspond to small amounts of a secondary phase(s). This phase could not be accurately identified from the powder diffraction database due to the weak intensities of the reflections. The possible secondary phases from the powders diffraction database might be Pr_5O_9 and/or Pr_2TiO_5 . However, the EDS analysis of the powders shows the presence of non-stoichiometric intermediate phases of different compositions than what was suggested from X-ray diffraction analysis. Figure 3(b) shows the backscattered electron (BSE) micrograph of the SrTiO_3 powder doped with Pr_6O_{11} . The observed secondary phases are highlighted with white arrows. Traces of Sr and Ti

FIG. 2. Crystal structures of (a) Pr_2O_3 with space group $P\bar{3}m1$, and (b) Pr_6O_{11} with space group $P2_1/c$.

FIG. 3. (a) X-ray diffraction pattern of SrTiO_3 powders doped with 1.5 at. % Pr using Pr_2O_3 and Pr_6O_{11} , respectively. $\blacktriangledown$ indicates the secondary phase reflections. (b) Electron backscattered (EBS) micrograph of the SrTiO_3 powder doped with 1.5 at. % Pr using Pr_6O_{11} as the doping source. EDS compositional analysis corresponding to the area in the red boxes is also shown. White arrows show the secondary phase particles present in the powder. (c) X-ray diffraction pattern of the bulk ceramics corresponding to the powders in (a). Inset shows the high-resolution diffraction pattern of (200) reflection of both bulk samples.

are observed in the praseodymium oxide secondary phase. The inset shows the magnified micrograph of a secondary phase particle possessing a clearly different morphology than the matrix. The compositional analysis of this particle suggests the Pr_2TiO_5 in which Pr is partially substituted with Sr. It is observed that the Pr content of the matrix (box at the bottom left of the micrograph) is close to the nominal 1.5 at. % concentration. Similar micrographs were observed for powder doped using Pr_2O_3 . Our experimental results suggest that under the synthesis condition of this work, reactions (1) and (2) follow similar reaction rates, despite the significantly different Gibbs

formation energy for Pr_2O_3 ($\Delta G_f^0 = -1720 \text{ kJ mol}^{-1}$) and Pr_6O_{11} ($\Delta G_f^0 = -5310 \text{ kJ mol}^{-1}$).

Figure 3(c) compares the diffraction pattern of the bulk ceramics prepared via spark plasma sintering from the two corresponding powders. The indexing was performed using DICVOL¹⁵ and N-TREOR¹⁶ programs, which are included in the PDXL software package. The reflections for the both samples prepared using Pr_6O_{11} and Pr_2O_3 , respectively, as the praseodymium doping source can be successfully indexed to $\text{Pm}\bar{3}\text{m}$ cubic lattice with a similar lattice parameter of $a = 3.908 \text{ \AA}$. This suggests the incorporation of similar valence states of Pr in SrTiO_3 lattice in both samples. The dominant oxidation state of Pr was previously indicated to be Pr^{3+} for ceramics doped using Pr_2O_3 .⁹

The possibility of the cubic to tetragonal transition, which has been reported before for SrTiO_3 upon incorporation of Pr with $x \geq 0.1$ (using Pr_6O_{11}),^{17–20} was also investigated. It is known that the cubic to tetragonal transition can be characterized by monitoring the peak splitting of the {200} reflection. High resolution x-ray diffraction measurements were performed at 30° – 50° with 0.001° step size and a scanning rate of $0.1^\circ/\text{min}$. Inset of Figure 3(c) shows the magnified view of the (200) reflection in both samples. No apparent peak splitting was observed, which suggests that the cubic $\text{Pm}\bar{3}\text{m}$ symmetry was maintained upon 1.5 at. % Pr doping.

Figure 4(a) shows the temperature dependence of the electrical conductivity, σ , for the two SrTiO_3 samples doped with Pr using Pr_2O_3 and Pr_6O_{11} , respectively. Both samples exhibit a degenerate semiconducting behavior. Very similar temperature-dependence is observed for both samples. Significantly larger values of electrical conductivity in these samples comparing to what is reported in the literature are a result of much improved carrier mobility in these samples arising from Pr-rich grain boundaries.

Figure 4(b) shows the Seebeck coefficient as a function of temperature. Very similar diffusive-like thermopower (in agreement with the degenerate semiconducting behavior) is observed for both samples and no sign of minority carrier contribution and bipolar effects are observed. Similar Seebeck values for both samples are in agreement with the similar Hall carrier concentrations ($\sim 1.4 \times 10^{21} \text{ cm}^{-3}$) shown in Figure 4(c). The almost temperature-independent carrier concentration suggests that the dopants are fully ionized above 20 K. Good agreement between the Hall carrier concentration, n_H ($\sim 1.4 \times 10^{21} \text{ cm}^{-3}$) and the “ideal doping” concentration ($\sim 1.25 \times 10^{21} \text{ cm}^{-3}$), which was calculated assuming each substitutional atom donates one electron to the system, suggests the incorporation of the majority of Pr dopants in Sr sites. This further supports the idea of the incorporation of Pr mainly as Pr^{3+} in both samples. It should be noted that the Hall carrier concentration includes the contribution from oxygen vacancies, which led to slightly higher n_H values than estimated by simple electron counting.

Figure 5 shows the temperature dependence of the thermoelectric power factor, PF. Values reported by Kovalevsky *et al.* for $\text{Sr}_{0.95}\text{Pr}_{0.05}\text{TiO}_3$ using Pr_6O_{11} as the doping source were also shown for comparison.²⁰ Similar power factor values and temperature-dependence were achieved in the whole

FIG. 4. Temperature dependence of (a) electrical conductivity, (b) Seebeck coefficient, and (c) Hall carrier concentration for SrTiO_3 ceramics doped using Pr_2O_3 and Pr_6O_{11} as the source of doping.

temperature range for the samples prepared in this work using Pr_2O_3 and Pr_6O_{11} as the Pr doping source. This observation is of great importance for practical application. The use of Pr_6O_{11} as the Pr doping source, instead of Pr_2O_3 , significantly reduces the cost of raw materials in these samples. Significantly larger values of power factor for these samples comparing to the values reported by Kovalevsky *et al.* can be mainly attributed to the non-uniform distribution of dopants, which was found to give rise to an improved carrier mobility. However, doping efficiency might be an additional

FIG. 5. Temperature dependence of thermoelectric power factor, PF, for $\text{Sr}_{0.925}\text{Pr}_{0.075}\text{TiO}_3$ ceramics doped using Pr_2O_3 and Pr_6O_{11} as the source of doping. Values reported in Ref. 20 for $\text{Sr}_{0.95}\text{Pr}_{0.05}\text{TiO}_3$ samples prepared using Pr_6O_{11} are also shown for comparison.

possible reason. Smaller values of Seebeck coefficient ($>20\%$) for similar nominal doping concentration might suggest a more efficient doping process, and hence, a larger carrier concentration for the samples prepared in this work.

In order to investigate the maximum achievable thermoelectric power factor and the corresponding optimum doping concentration for the samples prepared following our synthesis strategy, the electronic transport coefficients were calculated using the Boltzmann transport equation under the relaxation-time approximation. For a given carrier concentration, n , the Fermi energy, E_F , can be determined in a given energy range by self-consistently solving the following equation:

$$n = \int_0^\infty g(E)f(E)dE, \quad (3)$$

where $g(E)$ is the conduction band density-of-states and $f(E)$ the Fermi-Dirac distribution function,

$$g(E) = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} E^{1/2}, \quad (4)$$

$$f(E) = \left[\exp\left(\frac{E - E_F}{k_B T} \right) + 1 \right]^{-1}. \quad (5)$$

Here, m^* is the density of states effective mass, E_F the Fermi energy, $\hbar$ the reduced Plank's constant, and k_B the Boltzmann's constant. The electrical conductivity and Seebeck coefficient can then be described by the following expressions:²¹

$$\sigma = \frac{2e^2}{3m^*} \int_0^\infty \tau(E)g(E) \left(-\frac{\partial f(E)}{\partial E} \right) E dE, \quad (6)$$

$$\alpha = -\frac{1}{eT} \left[\frac{\int_0^\infty \tau(E)g(E) \left(-\frac{\partial f(E)}{\partial E} \right) E^2 dE}{\int_0^\infty \tau(E)g(E) \left(-\frac{\partial f(E)}{\partial E} \right) E dE} - E_F \right], \quad (7)$$

where e is the electron charge and $\tau(E)$ the momentum relaxation time for charge carriers. The thermoelectric power factor is then derived from the calculated electrical conductivity and Seebeck coefficient using $PF = \sigma \alpha^2 T$. Scattering from the ionized impurities and deformation potential of acoustic phonons were considered in the calculations. As it was previously reported, acoustic phonon scattering of charge carriers is the dominant scattering mechanism in SrTiO₃ above 700 K.²² The momentum relaxation-time for the scattering from ionized impurities is given by Brooks-Herring formula,^{23–25}

$$\tau_{II}(E) = \frac{16\pi\epsilon_s^2\sqrt{2m^*}}{Z^2e^4N_I} \times \left[\ln\left(1 + \frac{8m^*\lambda_S^2E}{\hbar^2}\right) - \frac{8m^*\lambda_S^2E/\hbar^2}{1 + 8m^*\lambda_S^2E/\hbar^2} \right]^{-1} E^{3/2}, \quad (8)$$

where ϵ_s is the static dielectric permittivity, Z is the number of charges per impurity, N_I is the concentration of charge impurities, which in an n-type semiconductors with fully ionized donors is equal to the electron density, and λ_S is the Debye screening length. For degenerate (i.e., highly doped) materials, the Thomas-Fermi approximation is used to calculate the screening length,²⁶

$$\lambda_S^{-2} = \frac{4\pi e^2 Z}{\epsilon_\infty} \int_0^\infty g(E) \left(-\frac{\partial f(E)}{\partial E} \right) dE, \quad (9)$$

where ϵ_∞ is the high frequency dielectric permittivity.

The momentum relaxation-time for the scattering of charge carriers from the deformation potential of acoustic phonons, $\tau_{ADP}(E)$, is calculated from the following equation:^{25,27}

$$\tau_{ADP}(E) = \frac{\hbar v_s^2 \rho}{\pi D_A^2 k_B T g(E)}, \quad (10)$$

where v_s is the longitudinal sound velocity, ρ the density, and D_A the acoustic deformation potential. The total momentum relaxation-time is then given by Mathiessen's rule,

$$\frac{1}{\tau(E)} = \frac{1}{\tau_{ADP}(E)} + \frac{1}{\tau_{II}(E)}. \quad (11)$$

Calculated transport coefficients as a function of carrier concentration at 775 K are shown in Figure 6. It is observed that the experimental results for Pr-doped SrTiO₃ ceramics⁹ are well described by a single parabolic band model with three conduction valleys at $\Gamma_{25'}$, a density-of-states effective mass of $m^* = 6.7m_e$ and an acoustic phonon deformation potential of $D_A = 6.7$ eV. The calculation is in excellent agreement (within 10%) with our experimental results for Pr-doped SrTiO₃ ceramics. It is observed that a carrier concentration of $\sim 2.1 - 2.3 \times 10^{-21} \text{ cm}^{-3}$ maximizes the thermoelectric power factor at 775 K, in accordance with the values experimentally determined.¹⁰ The calculations also predict a power factor of $\sim 1.8 \text{ W m}^{-1} \text{ K}^{-1}$ at 1175 K for $\sim 2.3 \times 10^{-21} \text{ cm}^{-3}$. The power factor at 1175 can be further

FIG. 6. Calculated transport coefficients, namely, absolute Seebeck coefficient, electrical conductivity, and thermoelectric power factor at 775 K as a function of carrier concentration (lines). Symbols represent the experimental results of the current work and the previous report⁹ as a function of room-temperature Hall carrier concentration.

improved to $\sim 2 \text{ W m}^{-1} \text{ K}^{-1}$ by increasing the carrier concentration to $\sim 4.5 \times 10^{-21} \text{ cm}^{-3}$. Therefore, higher doping levels are still desired in these sample, if experimentally possible, in order to fully realize the thermoelectric properties of SrTiO₃-based oxide ceramics. However, it was observed that Pr doping above $\sim 2.3 \times 10^{-21} \text{ cm}^{-3}$ could not be achieved experimentally.¹⁰ It would be of interest to investigate the possibility of further improvement in the power factor via double-doping.

In summary, a comparative study on the role of praseodymium doping source on the electronic transport in Pr-doped SrTiO₃ ceramics was investigated. It was observed that the electronic transport properties are independent of the choice of the doping source. This observation suggests that the intriguing electronic and thermoelectric properties of non-uniformly Pr-doped SrTiO₃ ceramics might not be correlated to the multivalent nature of Pr. A phenomenological model was used to estimate the maximum achievable power factor in these samples and the corresponding optimal carrier concentration. The results predict a power factor of $\sim 1.8 \text{ W m}^{-1} \text{ K}^{-1}$ at 1175 K for a carrier concentration of $\sim 2.3 \times 10^{-21} \text{ cm}^{-3}$, which can be further improved to $\sim 2 \text{ W m}^{-1} \text{ K}^{-1}$, provided that the carrier concentration can be increased to $\sim 4.5 \times 10^{-21} \text{ cm}^{-3}$. This might be achieved through co-doping the Pr-doped SrTiO₃ ceramics with another Sr- or Ti-site dopant.

ACKNOWLEDGMENTS

The authors wish to acknowledge the competitive faculty-initiated collaboration (FIC) grant from KAUST.

¹J. Schooley, W. Hosler, and M. L. Cohen, *Phys. Rev. Lett.* **12**, 474 (1964).

²J. H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y. L. Li, S. Choudhury, W. Tian, M. Hawley, B. Craigo *et al.*, *Nature* **430**, 758–761 (2004).

³D. Kan, T. Terashima, R. Kanda, A. Masuno, K. Tanaka, S. Chu, H. Kan, A. Ishizumi, Y. Kanemitsu, Y. Shimakawa *et al.*, *Nature Mater.* **4**, 816–819 (2005).

⁴T. Okuda, K. Nakanishi, S. Miyasaka, and Y. Tokura, *Phys. Rev. B* **63**, 113104 (2001).

- ⁵A. Durán, E. Martínez, J. Díaz, and J. Siqueiros, *J. Appl. Phys.* **97**, 104109 (2005).
- ⁶C. Liu, P. Liu, J.-p. Zhou, Y. He, L.-n. Su, L. Cao, and H.-w. Zhang, *J. Appl. Phys.* **107**, 094108 (2010).
- ⁷S. Okamoto, H. Kobayashi, and H. Yamamoto, *J. Appl. Phys.* **86**, 5594–5597 (1999).
- ⁸S. Itoh, H. Toki, K. Tamura, and F. Kataoka, *Jpn. J. Appl. Phys., Part 1* **38**, 6387 (1999).
- ⁹A. Mehdizadeh Dehkordi, S. Bhattacharya, T. Darroudi, J. W. Graff, U. Schwingenschlöggl, H. N. Alshareef, and T. M. Tritt, *Chem. Mater.* **26**, 2478 (2014).
- ¹⁰A. Mehdizadeh Dehkordi, S. Bhattacharya, J. He, H. N. Alshareef, and T. M. Tritt, *Appl. Phys. Lett.* **104**, 193902 (2014).
- ¹¹A. Mehdizadeh Dehkordi, S. Bhattacharya, T. M. Tritt, and H. N. Alshareef, *Bull. Am. Phys. Soc.* **57**, 12 (2012); also available at <http://meetings.aps.org/link/BAPS.2012.MAR.A17.12>.
- ¹²S. Bhattacharya, A. Mehdizadeh Dehkordi, S. Tennakoon, R. Adebisi, J. R. Gladden, T. Darroudi, H. N. Alshareef, and T. M. Tritt, *J. Appl. Phys.* **115**, 223712 (2014).
- ¹³S. Bhattacharya, A. Mehdizadeh Dehkordi, H. N. Alshareef, and T. M. Tritt, *J. Phys. D: Appl. Phys.* **47**, 385302 (2014).
- ¹⁴W. Kraus and G. Nolze, *J. Appl. Crystallogr.* **29**, 301–303 (1996).
- ¹⁵A. Boulouf and D. Louër, *J. Appl. Crystallogr.* **24**, 987–993 (1991).
- ¹⁶A. Altomare, C. Giacovazzo, A. Guagliardi, A. G. Moliterni, R. Rizzi, and P.-E. Werner, *J. Appl. Crystallogr.* **33**, 1180–1186 (2000).
- ¹⁷A. Durán, F. Morales, L. Fuentes, and J. M. Siqueiros, *J. Phys.: Condens. Matter* **20**, 085219 (2008).
- ¹⁸R. Garg, A. Senyshyn, H. Boysen, and R. Ranjan, *Phys. Rev. B* **79**, 144122 (2009).
- ¹⁹I. Sluchinskaya, A. Lebedev, and A. Erko, *J. Appl. Phys.* **112**, 024103 (2012).
- ²⁰A. Kovalevsky, A. Yaremchenko, S. Populoh, A. Weidenkaff, and J. Frade, *J. Appl. Phys.* **113**, 053704 (2013).
- ²¹G. S. Nolas, J. Sharp, and H. J. Goldsmid, *Thermoelectrics: Basic Principles and New Materials Developments* (Springer, 2001), Vol. 45.
- ²²S. Ohta, T. Nomura, H. Ohta, and K. Koumoto, *J. Appl. Phys.* **97**, 034106 (2005).
- ²³H. Brooks, *Phys. Rev.* **83**, 868 (1951).
- ²⁴B. R. Nag, *Electron Transport in Compound Semiconductors* (Springer-Verlag, Berlin, 1980), Vol. 11.
- ²⁵M. Lundstrom, *Fundamentals of Carrier Transport* (Cambridge University Press, 2009).
- ²⁶A. J. Minnich, H. Lee, X. W. Wang, G. Joshi, M. S. Dresselhaus, Z. F. Ren, G. Chen, and D. Vashaee, *Phys. Rev. B* **80**, 155327 (2009).
- ²⁷Y. I. Ravich, B. A. Efimova, and V. I. Tamarchenko, *Phys. Status Solidi B* **43**, 11–33 (1971).