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New insights on the synthesis and electronic transport in bulk polycrystalline Pr-doped SrTiO$_3$–x

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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$_2$O$_3$ versus Pr$_6$O$_{11}$) 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.

II. EXPERIMENTAL DETAILS

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

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different praseodymium oxides as the source of doping. Stoichiometric amounts of SrCO₃ powder (99.9%; Aldrich), TiO₂ nanopowder (99.5%; Aldrich), and Pr₂O₃ sintered lumps (99.9%; Alfa Aesar) for the first batch, and Pr₆O₁₁ 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:

\[
(1 - x)\text{SrCO}_3 + (x/2)\text{Pr}_2\text{O}_3 + \text{TiO}_2 \\
\rightarrow \text{Sr}_{1-x}\text{Pr}_x\text{TiO}_{3+\delta} + (1 - x)\text{CO}_2(g),
\]

(1)

\[
(1 - x)\text{SrCO}_3 + (x/6)\text{Pr}_6\text{O}_{11} + \text{TiO}_2 \\
\rightarrow \text{Sr}_{1-x}\text{Pr}_x\text{TiO}_{3+\delta} + (1 - x)\text{CO}_2(g).
\]

(2)

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 1400–1500°C for 5 min. Similar SPS conditions (load, heating/cooling rate, and pulse ratio) were employed for both samples. Densities, \( \rho \), of the bulk samples were determined using the Archimedes method and are all higher than 95% of their theoretical values. Rectangular bars (10 × 2 × 2 mm³) were cut from the disks for the measurements of electrical conductivity (\( \sigma \)) and Seebeck coefficient (\( \alpha \)). 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 ±3% and ±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 Kα 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 Pr₂O₃ and Pr₆O₁₁ powders used as the doping source as well as the corresponding simulated powder diffraction patterns, obtained with the PowderCell software package, are shown in Figure 1. Diffraction pattern of the Pr₂O₃ powder (light green in color) can be readily indexed to the Pr₂O₃ trigonal lattice (space group P3m1), while that of the Pr₆O₁₁ (dark brown-black in color) can be indexed to a tetragonal cell (space group P21/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 lattice of the intermediate phases (such as Pr₅O₉ or PrO₂) in the Pr-O phase diagram.

Diffraction profiles of Pr-doped SrTiO₃ powders prepared from Pr₂O₃ and Pr₆O₁₁ doping sources, respectively, are compared in Figure 3(a). Formation of SrTiO₃ phase is confirmed in both powders and the reflections can be indexed to a cubic lattice with Pm3m space group and a lattice parameter of \( a = 3.906 \text{ Å} \). 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 power diffraction database due to the weak intensities of the reflections. The possible secondary phases from the powders diffraction database might be Pr₅O₉ and/or Pr₂TiO₅. 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 SrTiO₃ powder doped with Pr₆O₁₁. The observed secondary phases are highlighted with white arrows. Traces of Sr and Ti

![Figure 1](image1.png)

**FIG. 1.** X-ray diffraction (XRD) profiles of fresh Pr₂O₃ and Pr₆O₁₁ powders, and the corresponding simulated diffraction patterns using PowderCell. ■ and ▲ show the reflections attributed to secondary phase(s).

![Figure 2](image2.png)

**FIG. 2.** Crystal structures of (a) Pr₂O₃ with space group P3m1, and (b) Pr₆O₁₁ with space group P21/c.
formation energy for Pr$_2$O$_3$ ($\Delta G^0_f = -1720 \text{ kJ mol}^{-1}$) and Pr$_6$O$_11$ ($\Delta G^0_f = -5310 \text{ kJ mol}^{-1}$).

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 DICVOL$^{15}$ and N-TREOR$^{16}$ programs, which are included in the PDXL software package. The reflections for the both samples prepared using Pr$_6$O$_11$ and Pr$_2$O$_3$, respectively, as the praseodymium doping source can be successfully indexed to Pm3m cubic lattice with a similar lattice parameter of $\alpha = 3.908 \text{ Å}$. 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$_2$O$_3$.$^7$

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$_6$O$_11$),$^{17–20}$ 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°/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 Pm3m symmetry was maintained upon 1.5 at. % Pr doping.

Figure 4(a) shows the temperature dependence of the electrical conductivity, $\sigma$, for the two SrTiO$_3$ samples doped with Pr using Pr$_2$O$_3$ and Pr$_6$O$_11$, 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 Sr$_{0.95}$Pr$_{0.05}$TiO$_3$ using Pr$_6$O$_11$ as the doping source were also shown for comparison.$^{20}$ Similar power factor values and temperature-dependence were achieved in the whole...
temperature range for the samples prepared in this work using Pr$_2$O$_3$ and Pr$_6$O$_{11}$ as the Pr doping source. This observation is of great importance for practical application. The use of Pr$_6$O$_{11}$ as the Pr doping source, instead of Pr$_2$O$_3$, 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 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:

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

(3)

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

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

(4)

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

(5)

Here, $m^*$ is the density of states effective mass, $E_F$ the Fermi energy, $h$ 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:

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

(6)

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

(7)

FIG. 4. Temperature dependence of (a) electrical conductivity, (b) Seebeck coefficient, and (c) Hall carrier concentration for SrTiO$_3$ ceramics doped using Pr$_2$O$_3$ and Pr$_6$O$_{11}$ as the source of doping.

FIG. 5. Temperature dependence of thermoelectric power factor, PF, for Sr$_{0.925}$Pr$_{0.075}$TiO$_3$ ceramics doped using Pr$_2$O$_3$ and Pr$_6$O$_{11}$ as the source of doping. Values reported in Ref. 20 for Sr$_{0.95}$Pr$_{0.05}$TiO$_3$ samples prepared using Pr$_6$O$_{11}$ are also shown for comparison.
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 \( PF = \sigma E S^2 T \). 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 SrTiO\(_3\) above 700 K.\(^{22}\) The momentum relaxation-time for the scattering from ionized impurities is given by Brooks-Herring formula\(^{23–25}\):

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

(8)

where \( \epsilon^* \) 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 \( \lambda_S \) is the Debye screening length. For degenerate (i.e., highly doped) materials, the Thomas-Fermi approximation is used to calculate the screening length:\(^{26}\)

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

(9)

where \( \epsilon_\infty \) is the high frequency dielectric permittivity.

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

\[
\tau_{\text{ADP}}(E) = \frac{\hbar v_s^* \rho}{\pi D_A^* k_B T g(E)},
\]

(10)

where \( v_s \) is the longitudinal sound velocity, \( \rho \) the density, and \( D_A \) the acoustic deformation potential. The total momentum relaxation-time is then given by Mathiessen’s rule,

\[
\frac{1}{\tau(E)} = \frac{1}{\tau_{\text{ADP}}(E)} + \frac{1}{\tau_{\text{II}}(E)}.
\]

(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 SrTiO\(_3\) ceramics\(^9\) are well described by a single parabolic band model with 3. This might be achieved through co-doping the Pr-doped SrTiO\(_3\) ceramics with another Sr- or Ti-site dopant.

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 report\(^1\) as a function of room-temperature Hall carrier concentration.

In summary, a comparative study on the role of praseodymium doping source on the electronic transport in Pr-doped SrTiO\(_3\) 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 SrTiO\(_3\) 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 SrTiO\(_3\) ceramics with another Sr- or Ti-site dopant.

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