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Synthesis of Non-uniformly Pr-doped SrTiO3 Ceramics and Their Thermoelectric Properties

--Manuscript Draft--

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Abstract:	We demonstrate a novel synthesis strategy for the preparation of Pr-doped SrTiO3 ceramics via a combination of solid state reaction and spark plasma sintering techniques. Polycrystalline ceramics possessing a unique morphology can be achieved by optimizing the process parameters, particularly spark plasma sintering heating rate. The phase and morphology of the synthesized ceramics were investigated in detail using X-ray diffraction, scanning electron microcopy and energy-dispersive X-ray spectroscopy. It was observed that the grains of these bulk Pr-doped SrTiO3 ceramics were enhanced with Pr-rich grain boundaries. Electronic and thermal transport properties were also investigated as a function of temperature and doping concentration. Such a microstructure was found to give rise to improved thermoelectric properties. Specifically, it resulted in a significant improvement in carrier mobility and the thermoelectric power factor. Simultaneously, it also led to a marked reduction in the thermal conductivity. As a result, a significant improvement (> 30%) in the thermoelectric figure of merit was achieved for the whole temperature range over all previously reported maximum values for SrTiO3-based ceramics. This synthesis demonstrates the steps for the preparation of bulk polycrystalline ceramics of non-uniformly Pr-doped SrTiO3.
Author Comments:	
Additional Information:	

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Question	Response
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CLEMSON
PHYSICS AND ASTRONOMY

February 21, 2015

Journal of Visualized Experiments

Dear Editor:

We received the editorial and reviewers' comments on the manuscript JoVE52869 entitled "*Synthesis of Non-uniformly Pr-doped $SrTiO_3$ Ceramics and Their Thermoelectric Properties*" by Arash Mehdizadeh Dehkordi, Sriparna Bhattacharya, Taghi Darroudi, Husam N. Alshareef and Terry M. Tritt. We would like to express our appreciation for your time and efforts spent on handling our manuscript. We have revised and improved the manuscript according to the comments. Detailed response to the comments and the changes made in the manuscript are included at the end of this letter.

If you have any further questions or if any of our coauthors or us, may provide any additional information, please do not hesitate to contact us. Thank you for considering this manuscript for publication in the *Journal of Visualized Experiments*.

Sincerely yours,

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The manuscript has been revised and improved according to the comments. The changes made in the revised manuscript are included under the Response and Change sections below and are highlighted in the manuscripts using "Track-Changes" function of Microsoft Word. We believe that the critique have greatly improved the quality and clarity of the manuscript. Our responses to these comments are as follows:

Science Editor:

Comment #1: Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues. The JoVE editor will not copy-edit your manuscript and any errors in the submitted revision may be present in the published version.
Response: The manuscript has been proofread.
Comment #2: Please add more details to your protocol steps. Please ensure you answer the "how" question, i.e., how is the step performed? Alternatively, add references to published material specifying how to perform the protocol action.
Response: Additional information along with the reference for detailed operation was added to the steps of the protocol to answer the "how" questions.
Comment #3: 1.12: Should the pellet be ground after this second calcination process before 1.13?
Response and Change: Thank you for pointing this out. This intermediate grinding was added as an extra step.
Comment #4: 2.10: Followed by what of the current?
Response and Change: This sentence was rephrased.
Comment #5: 3.3: How is the pellet cut? Also, please indicate in which steps each kind of cut piece is used. If the steps are not included in the protocol, please give citations for the analysis.
Response and Change: The pellet is cut using a diamond saw. This information was added to the description of this step (3.3).
Comment #6: 3.4.1: Please provide a reference on how to perform the DSC. Also, please add the experimental parameters: how much of the samples were used, how long, etc.
Response and Change: The reference of DSC and the details of the measurement parameters were added to the manuscript.
Comment #7: 3.6: Please provide a reference on how to operate the gold sputtering unit. How are the tiny holes cut?
Response and Change: The reference of DSC and the details of the measurement parameters were added to the manuscript.
Comment #8: Please revise the highlighting of the protocol text for filming. Only 2.75 pages of highlighted protocol text is permissible and there are currently 3.25 pages. Please include all relevant details that are required to perform the step in the highlighting. For example: If step 2.5 is highlighted for filming and the details of how to perform the step are given in steps 2.5.1 and 2.5.2, then the sub-steps where the details are provided must be highlighted. The Protocol is >3 pages highlighted. The authors could possibly unhighlight parts of section 3, which appear to be standard techniques without much stepwise detail (like 3.7).
Response and Change: The parts which are not of considered a critical step in the filming were unhighlighted according to editor's comment.
Comment #9: JoVE cannot publish manuscripts containing commercial language. This includes trademark symbols (™), registered symbols (®), and company names before an instrument or

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reagent. Please remove all commercial language from your manuscript and use generic terms instead. All commercial products should be sufficiently referenced in the Table of Materials and Reagents. There is unnecessary branding in 1.6 and 2.4 (Carver) and in 3.2.1 (MicroFlash).
Response and Change: Commercial language including the names of the suppliers of the equipment was removed from the manuscript.
Comment #10: Overall, the discussion is more results than method oriented. The discussion needs to focus on the methods in terms of the 5 discussion requirements. Which steps are critical? Are there any modifications or troubleshooting that typically occurs? How are these methods superior to the alternatives? Please discuss the limitations and critical steps of the technique. What are some future applications of the technique? Simply stating "this work may open new horizons and opportunities to other properties and applications" is not very informative.
Response and Change: The important step(s) were highlighted throughout the protocol. The future opportunities of this synthesis method were clarified. The key differentiating the synthesis strategy described in this protocol from previous reports in the literature were highlighted in the discussion.
Comment #11: JoVE reference format requires that DOIs are included, when available, for all references listed in the article. This is helpful for readers to locate the included references and obtain more information. Please note that often DOIs are not listed with PubMed abstracts and as such, may not be properly included when citing directly from PubMed. In these cases, please manually include DOIs in reference information.
Response and Change: The DOIs of the references which were available were included in the reference list. We'd appreciate if the JoVE template can be modified to include the DOIs for future publications.

Reviewer #1:

Comment #1: Line 70 Reference is not defined.
Response: The reference to room-temperature electron mobility of $SrTiO_3$ had already been cited. It seems that Microsoft Word cross-referencing had a problem in updating the reference number. This issue was resolved.
Comment #2: Line 92 Reference is not defined.
Response and Change: Reference 12 has been cited for "spark plasma sintering technique".
Comment #3: Line 351 Reference is not defined.
Response and Change: Reference 13 has been cited for the results reported in Line 351.
Comment #4: Figures 2(b) and 2(c) are missing.
Response: Figures 2(b) and 2(c) have already been included in the Fig. 2.eps file uploaded before. It seems like the online pdf compilation system somehow did not incorporate the image.
Comment #5: Y-axis unit of Fig. 3(b) should be microV K^{-1} not mV K^{-1}.
Response and Change: Fig. 3 (b) was modified. It seems that the "mu" font had been change during file conversion.
Comment #6: Line 352-353 The authors mention that … whole temperature range over all previously reported maximum values were achieved …. However, no reference is cited.
Response: We thank the review for his/her comment. However, since the reported values were higher than reported in "all" previous publications we believe that the citations of selected

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previous reports might be unnecessary. However, Fig. 3 compares the results to some of the highest values reported in the literature. The references are included in the caption.

Reviewer #2:

Comment #1: Line 114: Researchers generally use the powder of Pr_2O_3 for synthesis. So the authors should shortly explain why the Pr_2O_3 sintered lump was used in the manuscript.
Response: We thank the reviewer for his/her comment. However, to the best of our knowledge researchers use both forms of Pr_2O_3. Alfa Aesar only supplies Pr_2O_3 in "sintered-lump" form which was chosen due to its competitive price comparing to the Pr_2O_3 supplied by Sigma-Aldrich. Nevertheless, our recent publication (Dehkordi *et al.*, J. Appl. Phys. **117** (2015) 055102) shows that the thermoelectric properties following the synthesis protocol presented in the manuscript is independent of the choice of Pr doping source.

Reviewer #3:

Comment #1: Line 70: Give references to the low carrier mobility of single crystals.
Response and Change: The reference to room-temperature electron mobility of $SrTiO_3$ had already been cited. It seems that Microsoft Word cross-referencing had a problem in updating the reference number. This issue was resolved.
Comment #2: Line 33-34: Power factor is already a defined term in thermoelectrics. The authors should change the phrase. "We herein define the numerator as the power
factor..."
Response: Traditionally, the thermoelectric power factor is defined in the Z context (not ZT) as $\sigma\alpha^2$ where σ is the electrical conductivity, and α the Seebeck coefficient. Researchers still generally define the power factor this way. However, here we define the power factor as $\sigma\alpha^2T$. Not only this definition portrays the actual temperature dependence of the electronic properties incorporated in ZT calculation but it also gives the SI SI of W/m-K similar to that of thermal conductivity.
Comment #3: Line 92: provide references to the conventional sintering.
Response and Change: Reference to "conventional sintering" had already been cited. It seems that the Microsoft Word cross-referencing had a problem in updating the reference number. This issue was resolved.
Comment #4: Line 118 and 120: "Weighted" powder should be "weighed" powder.
Response and Change: Thank you for pointing this out. The typo was fixed.
Comment #5: Line 123-124: 1.4) the step is not clearly understood. How does mixing of TiO_2 powder cause reduction of volume? Do the mixing process involve manual mixing or using any particular mixing instrument?
Response: The mixing can be done either manually or with a commercial tabulator/mixer. Since the TiO_2 is a nanopowder mixing help locally cold-pressing the powder to reduce the overall volume of the portion used so it can be fitted in the stainless steel die. This part was removed to avoid confusing the reader.
Comment #6: Line 131: "green body" is an unscientific language. Replace it with a more appropriate noun.

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Response: “Green body” is the technical term used primarily by ceramist for unsintered or unfired ceramics, which has been used extensively in the journal publications as well as the encyclopedia of advanced materials.

Comment #7: Line 138-141: 1.9) Define calcination first and then use the term. the phrase "let it reside.." is inappropriate in scientific papers. Replace it with clear words like "kept it at the elevated temperature.."

Response and Change: Calcination is a known technical term used by researchers in ceramics sciences and processing referring to the thermal treatment (firing) step in the solid-state reaction synthesis of ceramics. We do not believe this term needs to be defined here. The text was modified according to the reviewer’s comment on “let it reside…”.

Comment #8: Line 144: Has turbulator been used before during mixing the powders? If yes, mention.

Response and Change: Yes. The use of turbulator/mixer was added to step 1.4.

Comment #9: Line 267-271: The step describing the use of scotch-tape is not clear. The author should elaborate on this point for clear understanding to the general readers.

Response and Change: This step was clarified to explain the use of scotch tape as a stencil for the gold sputtering of the contacts.

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TITLE:
Synthesis of Non-uniformly Pr-doped $SrTiO_3$ Ceramics and Their Thermoelectric Properties

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KEYWORDS:
Oxide Thermoelectrics, Praseodymium, $SrTiO_3$, Enhanced Figure of Merit, Enhanced Power Factor, N-type Semiconductor, Mobility Enhancement, Grain Boundary Engineering

SHORT ABSTRACT:
A protocol for the synthesis and processing of polycrystalline $SrTiO_3$ ceramics doped non-

uniformly with Pr is presented along with the investigation of their thermoelectric properties.

LONG ABSTRACT:

We demonstrate a novel synthesis strategy for the preparation of Pr-doped $SrTiO_3$ ceramics via a combination of solid state reaction and spark plasma sintering techniques. Polycrystalline ceramics possessing a unique morphology can be achieved by optimizing the process parameters, particularly spark plasma sintering heating rate. The phase and morphology of the synthesized ceramics were investigated in detail using X-ray diffraction, scanning electron microcopy and energy-dispersive X-ray spectroscopy. It was observed that the grains of these bulk Pr-doped $SrTiO_3$ ceramics were enhanced with Pr-rich grain boundaries. Electronic and thermal transport properties were also investigated as a function of temperature and doping concentration. Such a microstructure was found to give rise to improved thermoelectric properties. Specifically, it resulted in a significant improvement in carrier mobility and the thermoelectric power factor. Simultaneously, it also led to a marked reduction in the thermal conductivity. As a result, a significant improvement (> 30%) in the thermoelectric figure of merit was achieved for the whole temperature range over all previously reported maximum values for $SrTiO_3$-based ceramics. This synthesis demonstrates the steps for the preparation of bulk polycrystalline ceramics of non-uniformly Pr-doped $SrTiO_3$.

INTRODUCTION:

Oxide thermoelectrics were shown to be promising candidates for high-temperature thermoelectric applications, from stability and cost perspectives to electronic transport properties. Among the n-type oxide thermoelectrics, highly doped strontium titanate (STO) has attracted much attention due to its intriguing electronic properties. However, a large total thermal conductivity ($\kappa \sim 12$ $Wm^{-1}K^{-1}$ at 300 K for single crystals)[1] and a low carrier mobility ($\mu \sim 6$ cm^2V^{-1} s^{-1} at 300 K for single crystals)[1] detrimentally affect the thermoelectric performance which is evaluated by a dimensionless figure of merit, $ZT = \alpha^2\sigma T/\kappa$, where α is the Seebeck coefficient, σ the electrical conductivity, T the absolute temperature in Kelvin, and κ the total thermal conductivity. We herein define the numerator as the power factor, $PF = \alpha^2\sigma T$. In order for this oxide thermoelectric material to compete with other high-temperature thermoelectrics (such as SiGe alloys), a more pronounced increase in the power factor and/or decrease in lattice thermal conductivity are required.

The majority of the experimental studies in order to improve the thermoelectric properties of STO have mainly focused on the reduction of thermal conductivity through strain-field and mass fluctuation scattering of phonons. These attempts include: (i) Single- or double-doping of the Sr^{2+} and/or Ti^{4+} sites, as the main efforts with respect to this direction,[2,3] (ii) Synthesis of natural superlattice Ruddlesden–Popper structures in order to further reduce the thermal conductivity through insulating SrO layers,[4] and (iii) Composite engineering by addition of a nanosized second phase.[5] However, up until recently, no enhancement strategy has been reported to substantially increase the thermoelectric power factor in these oxides. The reported maximum power factor (PF) values in bulk single- and poly-crystalline STO have been confined to an upper limit of $PF < 1.0$ $Wm^{-1}K^{-1}$.

A variety of synthesis approaches and processing techniques have been employed to implement the ideas attempted above. The powder synthesis routes include conventional solid-state reaction,[6] sol-gel,[7] hydrothermal,[8] and combustion synthesis,[9] whereas conventional sintering,[6] hot pressing[10] and recently spark plasma sintering[12] are among the common techniques used to densify the powders into bulk ceramics. However, for a similar dopant (e.g. La) and doping concentration, the resulting bulk ceramics exhibit a range of electronic and thermal transport properties. This is in large due to the strongly process-dependent defect chemistry of $SrTiO_3$ which results in synthesis-dependent properties. There is only a handful of reports optimizing the synthesis and processing parameters to benefit thermoelectric transport. It is worth mentioning that due to the very small phonon mean free path in $SrTiO_3$ (l_{ph}~2 nm at 300K),[11] nanostructuring is not a viable option for the improvement of the TE performance of bulk STO ceramics primarily through the reduction of the lattice thermal conductivity.

Recently, we reported more than 30% improvement in the thermoelectric figure of merit in non-uniformly Pr-doped $SrTiO_3$ ceramics originating from a simultaneously enhanced thermoelectric power factor and reduced thermal conductivity.[12,13] In this detailed video protocol, we present and discuss the steps of our synthesis strategy for the preparation of these Pr-doped STO ceramics exhibiting improved electronic and thermoelectric properties.

PROTOCOL:

1. Preparation of Pr-doped $SrTiO_3$ Powder

1.1) In order to prepare 10 g of $Sr_{0.95}Pr_{0.05}TiO_3$ powder, weigh the stoichiometric amounts of $SrCO_3$ powder (7.53407 g), TiO_2 nanopowder (4.28983 g), and Pr_2O_3 sintered lump (0.44299 g) following the reaction for $x = 0.05$

$$(1-x)\mathrm{SrCO_3} + \left(\frac{x}{2}\right)\mathrm{Pr_2O_3} + \mathrm{TiO_2} \rightarrow \mathrm{Sr_{1-x}Pr_xTiO_{3-\delta}} + (1-x)\mathrm{CO_2} \qquad (1)$$

1.2) Grind the weighed Pr_2O_3 sintered lumps to fine particles using an agate mortar and pestle.

1.3) Add the weighed $SrCO_3$ powder and TiO_2 nanopowder to the Pr_2O_3 and continue grinding and mixing using an agate mortar and pestle until a visually homogenous powder is achieved.

1.4) Load the ground powder into a glass jar and mix using a turbulator for 30 minutes to homogenize the mixture.

1.5) Load the resulting mixed powder into a meticulously cleaned and polished stainless steel die (1 inch in diameter) and sandwich it between two stainless steel plungers.

1.6) Cold press the powder using a press under an approximately 1 metric ton load.

1.7) Eject the cold-pressed pellet by placing the die on a hollowed stainless steel cylinder and

pushing the plungers and the pellet out from the top using a pushing rod. Upon ejection of the cold pressed pellet (green body) from the die, clean any contamination on the circumferential surface of the pellet by gently covering the pellet with a small piece of scotch-tape and removing a thin layer by ripping the tape.

1.8) Place the pellet vertically in an alumina boat filled with commercially purchased $SrTiO_3$ powder as the barrier between the alumina boat and the cold press pellet.

1.9) Place the boat in a tube furnace, heat up to 1300 °C in 3 hours and keep it at this temperature for 15 hours. Allow the pellet to cool down to room temperature inside the furnace when the calcination is over. This step is referred to as the "calcination process" thereafter.

1.10) Grind the pellet using the agate mortar and pestle and load the resulting powder into a glass jar for further mixing using the turbulator.

1.11) Load the powder into the stainless steel die and cold pressed under an approximately 3 metric tons of load.

1.12) Repeat the step 1.9 one more time at 1400 °C in 3 hours and keep it at this temperature for 20 hours.

1.13) Grind the pellet using the agate mortar and pestle.

1.14) Repeat steps 1.11, 1.12, and 1.13 one more time for the solid state reaction to reach completion.

2. Preparation of Bulk Polycrystalline Pr-doped $SrTiO_3$ Ceramic

2.1) Weigh 1.6 g of the as-prepared powder (for a disk 2 mm thick and 12.7 mm in diameter).

2.2) Prepare circular graphoil pieces to cover the top and bottom interface of the sandwiched powder and graphite plungers in the graphite die. Also, prepare another rectangular graphoil piece to cover the inner wall of the graphite die.

2.3) Load the as-prepared powder into a graphite die (12.7 mm in inner diameter) and sandwich the powder between two graphite plungers of the same size. Drill a 2-mm hole in the middle of the length of the graphite die and from the outer surface of the die to about 2 mm of the inner surface for temperature reading.

Note: Adjust the length of the graphite plungers remaining outside the die and position the center of the sandwiched powder cylinder where the hole is placed to get an accurate temperature reading. The faces of the graphite plungers need to be meticulously leveled during the machining of the pieces. Any misalignment can result in the cracking of the sintered pellet

during spark plasma sintering.

2.4) Cold-press the powder gently (load < 200 kg) using a press prior to mounting on the spark plasma sintering plate inside the chamber. Use flat polished stainless steel support plates between the top and bottom plungers and the press stage to avoid damaging the graphite plungers.

2.5) Wrap a piece of graphite felt around the die for insulation and secure it with graphite yarn. Devise a window on the graphite felt by cutting a rectangular piece of the felt where the temperature reading hole is placed on the die.

2.6) Place the loaded graphite die and plungers in the spark plasma sintering chamber. Move the stage to the final position.

2.7) Focus and align the Pyrometer target circle on the temperature reading hole of the die. Make sure the emissivity setting of the pyrometer is set for graphite.

2.8) Close the chamber and put a 7.7 kN load (approximately 60 MPa) on the sample. Vacuum and purge the chamber with Ar three times and leave the chamber under dynamic vacuum of 6 Pa.

2.9) Increase the temperature by increasing the current (manually or using a program). Use 250 A min^{-1} (corresponding to approximately 300-400 $^{\circ}C$ min^{-1}) for the optimized samples. This is the most important step of the spark plasma sintering process.

2.10) Keep the temperature at 1500 °C for 5 min by manually adjusting the current or using the program. At the end of the 5 min holding period, shut the current off and quickly release the 7.7 kN load to avoid cracking the sample during the cooling down. Let the sample cool to room temperature inside the chamber.

2.11) Release the bulk pellet from the graphite die gently using the cold press. This is done by placing the graphite die on a hollowed steel cylinder and ejecting the pellet and the graphite plungers using a steel pushing rod from the top.

2.12) Remove the graphoil on top and bottom faces of the pellet as well as the circumferential surface using a sharp razor blade.

2.13) Polish the sample using a rough sand paper (400 grid) down for 0.3-0.5 mm from each side to assure the complete removal of the graphoil. Clean the sample with acetone.

3. Characterization of Electronic and Thermal Transport Properties of Bulk Ceramics

3.1) Determine the density of the ceramic disk, ρ, using the Archimedes method.

3.1.1) Measure the weight of the sample, W_{dry}, and then the weight of the sample submerged in water, W_{wet}, on a stabilized density measurement system and calculate the Archimedes density from

$$\rho = \frac{W_{\mathrm{dry}}}{W_{\mathrm{dry}} - W_{\mathrm{wet}}} \rho_{\mathrm{water}} \qquad (2)$$

where ρ_{water} is the density of the water at the measurement temperature (e.g. equals 1 g cm^{-3} at 300K).[14]

3.2) Measure the thermal diffusivity of the sample, d, using the transient laser-flash technique under a 75 ml min^{-1} flow of Ar. Measure the thickness of the sample, *L*, accurately first using a digital micrometer.

Note: Parallel-faced samples with different sizes and shapes (e.g. round discs 12.7 mm in diameter or square 10 x 10 mm^2 disks) and thicknesses between 0.5 and 5 mm can be easily measured.

3.2.1) In the laser-flash thermal diffusivity technique, irradiate one face of the sample by a short (~1 ms) laser pulse and record the temperature rise on the opposite face by an infra-red detector. Then calculate thermal diffusivity by the laser-flash interface software from the thickness of the sample and the temperature rise-time profile using the Parker equation[15]

$$d = 0.138 \frac{L^2}{t_{1/2}} \qquad (3)$$

where *L* is the thickness of the disk and $t_{1/2}$ is the half-time of the maximum temperature rise of the other side of the sample.

Note: The Parker model[15] assumes ideal conditions of adiabatic sample and instantaneous pulse heating, other models have been proposed over the years, which account for various losses in the measurement such as heat losses, finite pulse duration, non-uniform pulse heating and nonhomogeneous structures. We have used the Cowan model[16] with pulse correction which is one of the most advanced methods. It should be noted that in order to maximize the amount of thermal energy transmitted from the front surface and to maximize the signal observed by the IR detector, the sample surfaces must be highly emissive. Usually this requires the application of a thin coating of graphite to the sample surfaces. An uncertainty of 2-5% in the measurement of thermal diffusivity exists, arising from the determination of dimension.[17]

3.3) Cut the disk pellet using a diamond saw into rectangular bars, 2 x 2 x 10 mm^3, electrical conductivity and Seebeck coefficient measurements as well as a square disk, 4 x 4 x 1.5 mm^3 for high-temperature specific heat and a thin rectangular piece, 8 x 5 x 1 mm^3 for Hall measurements.

3.4) Measure the specific heat, C_p, of the sample on the flat and mirror-polished square piece (4 x 4 x 1.5 mm^3) using a differential scanning calorimetry (DSC) under argon flow.[18].

3.4.1) Use a heating rate of 5 K min^{-1} up to 40°C for an isothermal hold for 10 min to allow the

sample to reach thermal equilibrium followed by 20 K min^{-1} heating rate up to 500°C, with an exact cooling rate which followed. Perform the measurement under the flow of argon (50 mL min^{-1} is suggested).

Note: Due to the sensitivity of the method used for analysis, conduct three measurements to determine the heat capacity including (1) a baseline measurement to subtract the background, (2) measurement of the specific heat of a standard material (such as sapphire) with a known C_P, and (3) measurement of the specific heat of the sample. Ensure that samples are flat and mirror-polished in order to make an ideal contact with the bottom of the measurement crucible (Pt/Rh pans with Al_2O_3 crucibles used in this work). More details on the exact structure of the DSC stage, a comparison of the DSC techniques to others, and exact instructions for measuring a sample can be found in various sources.[19]

3.5) Calculate the high-temperature thermal conductivity, κ, of the sample from the measured values of thermal diffusivity, *d*, the specific heat, C_P, and the density, ρ using[20]

$$\kappa = \rho d C_P. \qquad (4)$$

3.6) Gold plate the probes contact points (4 contacts) on the 2 x 2 x 10 mm^3 piece cut from the sample to alleviate the contact resistance issues.

3.6.1) In order to sputter gold only on the desired contact areas, wrap a scotch-tape around the 2 x 2 x 10 mm^3 sample to use as a stencil. Leave the 2 x 2 mm^2 faces un-covered. Using a razor blade, cut out 2 very small holes (approximately 1 mm in diameter) in the middle of the 2 x 10 mm^2 face along a line separated by the probes distance.

3.6.2) Sputter a ~ 200 nm-thick gold film using a bench-top gold sputtering unit.[21]

3.7) Measure the electrical transport properties, namely the electrical conductivity and Seebeck coefficient) of the sample as a function of temperature[22,23].

3.7.1) Measure electrical conductivity using the four-terminal method. Measure the Seebeck coefficient on the same setup using the measurements of temperature and voltage via the two middle thermocouple "probes". Measure the distance between these two probes using a digital microscope. More details on the electrical transport measurements can be found elsewhere.[22,23]

3.8) Measure the Hall carrier concentration as a function of temperature on the 8 x 5 x 1 mm^3 sample using a Physical Properties Measurement System.[24]

REPRESENTATIVE RESULTS:

X-ray diffractions patterns were collected for the as-prepared powders and the corresponding bulk ceramics as a function of Pr-content (Figure 1) in order to study the effect of Pr-doping on the $SrTiO_3$ lattice, solubility of Pr in $SrTiO_3$ and the formation of secondary phase(s). The

patterns confirm the formation of $SrTiO_3$ phase in all the as-prepared powders where the reflections can be indexed to a cubic lattice with $Pm\bar{3}m$ space group (Figure 1a). The monotonic change in the indexed lattice parameter from a = 3.906 for x = 0 (undoped) with increasing Pr content confirms the distortion of the lattice upon incorporation of smaller Pr^{+3} ions in Sr^{2+} sites. Weak reflections were also observed for x > 0.05, corresponding to the intermediate praseodymium oxide phase (e.g. Pr_5O_9), which increase intensity with increasing nominal Pr concentration (Figure 1b). It was found that by optimizing the SPS heating rate the reflections corresponding to the secondary phase(s) are fully disappeared (Figure 1c, d).

A synthesis-structure-property relationship study was conducted in order to understand the effect of the SPS heating rate and the observed secondary phase on the electronic transport properties. Scanning electron micrographs were acquired in conjunction with energy-dispersive X-ray spectra to investigate the effect of the synthesis and densification parameters, particularly spark plasma sintering heating rate, on the morphology and the chemistry of the grains and grain boundaries (Figure 2). Synthesis-(micro) structure-property relationship was investigated by monitoring the temperature-dependence of electronic transport properties of the bulk ceramics (Figure 2). It was found that electrical conductivity can be significantly increased through the optimization of the SPS heating rate (Figure 2a). This improvement was attributed to a marked enhancement in the carrier mobility since similar Seebeck coefficient and carrier concentration values were obtained for samples densified under different heating rates (Figure 2a, inset). Scanning electron micrographs have shown that the Pr-rich secondary phase present in the as prepared powder (Figure 2b, inset) can partially dope the grain boundary region during the SPS process (Figure 2b). By the appropriate optimization of the SPS heating rate, the grain boundary region can be fully doped with Pr, in which case an enhancement in the carrier mobility is observed (Figure 2c).

Electronic and thermal transport properties of the bulk ceramics prepared with a high SPS heating rate of 300 °C min^{-1} were measured as a function of temperature and Pr content in order to calculate the overall thermoelectric figure of merit (Figure 3). All samples exhibit a degenerate semiconducting behavior (i.e. metallic-like) for electrical conductivity (Figure 3a) and a corresponding diffusive-like thermopower (Figure 3b). Large thermoelectric power factor > 1 W m^{-1} K^{-1} was observed for ceramics with x > 0.075 in a broad temperature range reaching a maximum of 1.3 W m^{-1} K^{-1} for x = 0.15, corresponding to 3 at.% Pr (Figure 3c). Simultaneously, a monotonic reduction in thermal conductivity was observed with increasing Pr up to x = 0.15 (Figure 3d). The optimum nominal Pr concentration was found to be x = 0.15 for these samples.[Error! Bookmark not defined.] More than 30% improvement in the dimensionless thermoelectric figure of merit (ZT) for the whole temperature range over all previously reported maximum values were achieved as a result of the simultaneous enhancement in the thermoelectric power factor and reduction in the thermal conductivity (Figure 3e).[13] Maximum ZT value of 0.35 was obtained at 500°C. If the measurements are to be performed under a highly reducing atmosphere, maximum ZT values above 0.6 are predicted at 1000°C by fitting the experimental electronic and thermal transport data. The possibility of further improvement of the power factor at these temperatures, and hence ZT also exist if the carrier concentration can be further increased.[30]

Figure 1: X-ray diffraction profiles. (a) X-ray diffraction (XRD) profiles of $Sr_{1-x}Pr_xTiO_{3-\delta}$ powders before SPS as a function of nominal Pr content. (b) Magnified view of the dashed rectangle in (a), (c) XRD profiles of $Sr_{1-x}Pr_xTiO_{3-\delta}$ with x = 0.075 before SPS (Powder) and after high-heating-rate SPS (Bulk Ceramic). Photographs of cold-pressed powder after solid-state reaction and the corresponding SPSed ceramic are shown. (d) Magnified view of the dashed rectangle in (c). Reprinted with permission. [12]

Figure 2: Effect of SPS heating rate. (a) Temperature dependence of electrical conductivity and Seebeck coefficient (inset) for $Sr_{1-x}Pr_xTiO_{3-\delta}$ ceramics with x = 0.075 processed using two different SPS heating rates of 100 °C $min^{-1}$and 300 °C min^{-1}, respectively. (b) Backscattered electron (BSE) micrograph of the ceramic made under 100 °C min^{-1} SPS. A typical Pr spectrum of the EDS line scan across a PrO_y particle is shown. (c) Backscattered electron micrograph of the ceramic made under a 300 °C min^{-1} SPS heating rate. A typical Pr spectrum of EDS line scan across two grains, grain 1 and grain 2, is shown. The inset depicts the BSE micrograph of the $Sr_{0.95}La_{0.05}TiO_3$ ceramic prepared following the same recipe. Reprinted with permission. [12]

Figure 3: Thermoelectric transport properties. Temperature dependence of (a) electrical conductivity (σ), (b) Seebeck coefficient (α), (c) power factor (defined as PF= α2σT), (d) total thermal conductivity and (e) figure-of-merit, ZT for $Sr_{1-x}Pr_xTiO_{3-\delta}$ ceramics as a function of Pr content. Temperature dependence of reported maximum ZT values in the literature is shown for comparison.[2,25-28,] Reproduced with permission. [12,13]

DISCUSSION:

In this protocol, we have presented the steps of the synthesis strategy in order to successfully prepare bulk polycrystalline Pr-doped $SrTiO_3$ ceramics exhibiting improved electronic and thermoelectric properties. The main steps of the protocol include (i) the solid-state synthesis of the doped $SrTiO_3$ powder in air under atmospheric pressure and (ii) taking advantage of the capabilities of spark plasma sintering technique to densify the as-prepared powder into high-density bulk ceramics and at the same time to further dope the grain boundaries of the sample with Pr. It was demonstrated that by applying a high SPS heating rate (300-400 $^{\circ}C\ min^{-1}$) the reflections in the X-ray diffraction patterns corresponding to the secondary phase(s) are fully disappeared (Figure 1c, d). The high heating rate is one of the key differences of this synthesis strategy with previous reports in the literature.[17] Complete incorporation of Pr dopants in Sr sites, which lead to measured carrier concentration values corresponding to the nominal doping values[12], is one of the main accomplishments of this synthesis strategy. As a result, higher carrier concentration values were observed for the samples prepared in this work comparing to the values reported in the literature for the samples prepared using other methods with same nominal doping concentrations. Taking advantage of the highly-reducing atmosphere of spark plasma sintering chamber (graphite die under dynamic vacuum and high heating rate) to reduce the oxide powder in order to create oxygen vacancies as another source of electron doping also differentiates this protocol from other samples reported in the literature prepared under Ar[29] or forming gas (5-10% H in Ar)[29] atmospheres.

Furthermore, it was observed that by applying a high SPS heating rate, secondary phases, which are primarily praseodymium oxide, can locally dope the grain boundary regions. This non-uniform doping of the ceramic samples resulted in the observation of an unexpected marked improvement in the carrier mobility, thermoelectric power factor as well as a significant reduction in the total thermal conductivity. The experimental data suggest that the observed enhancement is correlated to the unique microstructure of the ceramics and the presence of Pr-rich boundary regions. Such boundaries were not observed for the $SrTiO_3$ ceramics doped with other dopants such as La (Figure 2c, inset) or prepared with other synthesis methods reported in the literature. A recent theoretical study by Dawson and Tanaka attempts to explain this observation (i.e. why Pr-doping induces core–shell formation and La-doping does not) by investigating the local structure and energetics of Pr- and La-doped $SrTiO_3$ grain boundaries.[30] Their calculations show a far stronger energetic benefit for Pr-doping of grain boundaries than La-doping. Since the electronic transport results could not be explained by effective medium theory,[12] it is believed that a charge transfer mechanism is likely to be involved in the carrier mobility improvement.

The results prove that the strategy can be applied as a method to synthesize in-situ composite structures particularly of the core-shell type structure. However, the efficiency of the non-uniform doping depends on the nature of the constituent phases of the composite. This method is limited by the melting point of the phases present in the material. High heating rates of 300-400 $^{\circ}C\ min^{-1}$ can locally melt the material under mechanical pressure and either crack the sample or change the properties. Therefore, this protocol is a good synthesis strategy to be implemented to other oxides due to their high-temperature stability. Caution should be exercised when the method is applied to other thermoelectric materials. The conditions of spark plasma sintering technique need to be optimized before applying the strategy to other materials systems. It should be noted that due to the high heating rates applied, significant grain growth is expected if the densification part of the protocol is employed on nanosctructured powders.

Future work to modify the current protocol in order to further improve the thermoelectric properties will focus on the simultaneous optimization of the effect of the mechanical load (60 MPa in this protocol), the SPS soaking temperature, and soaking time to further reduce the thermal conductivity, improve the power factor, and to improve the success rate of the preparation of crack-free samples.

In conclusion, we have demonstrated the synthesis approach for the preparation of bulk polycrystalline Pr-doped $SrTiO_3$ ceramics with Pr-rich grain boundaries exhibiting significantly improved electronic and thermoelectric properties. The synthesis strategy utilized in this work may open new horizons and opportunities to other properties and applications of this broadly functional perovskite where higher carrier mobility is desired. Moreover, the grain boundary engineering using spark plasma sintering demonstrated in this work can be implemented in other oxide materials to modify the physical properties.

DISCLOSURES:

The authors have nothing to disclose.

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Figure 1

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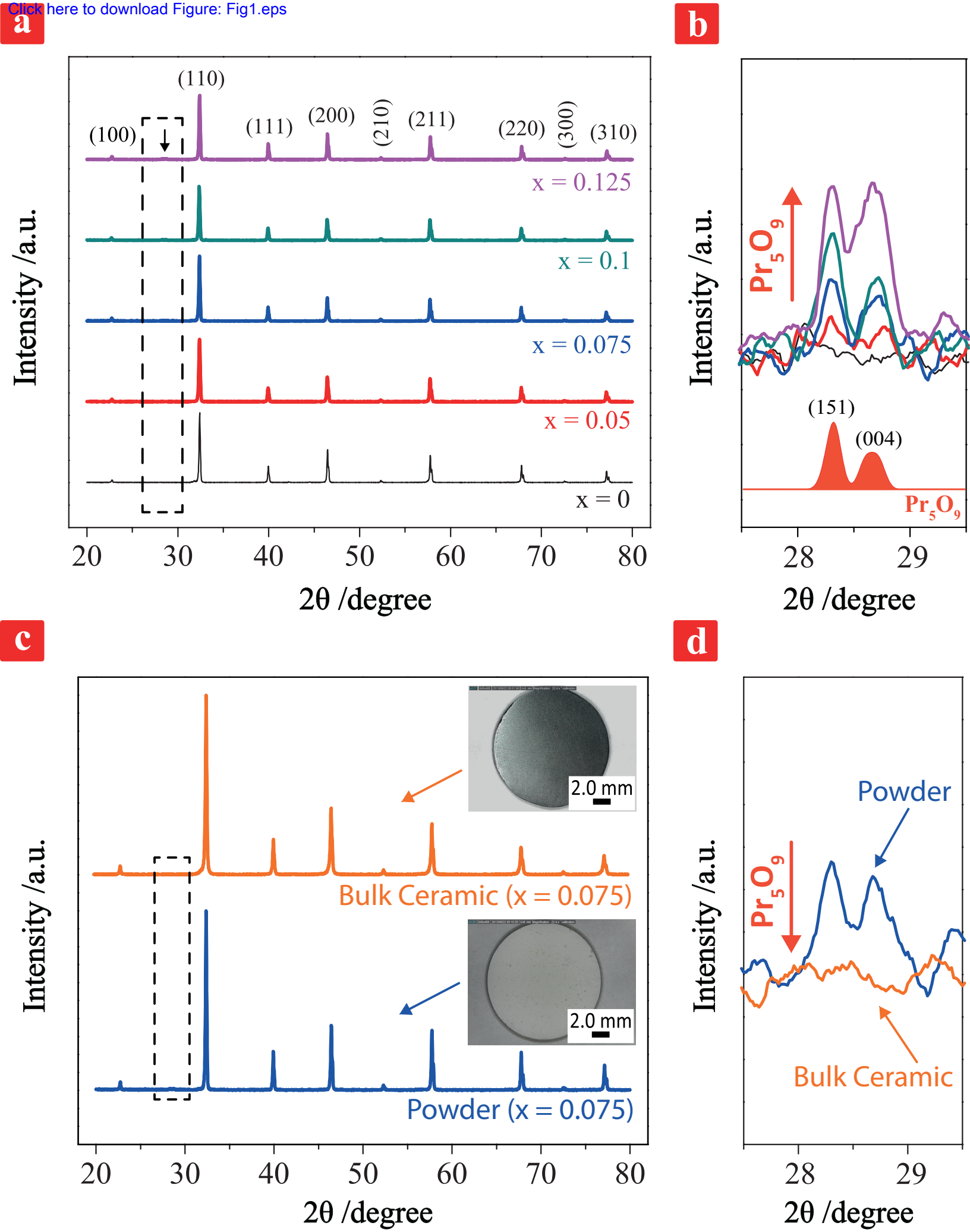

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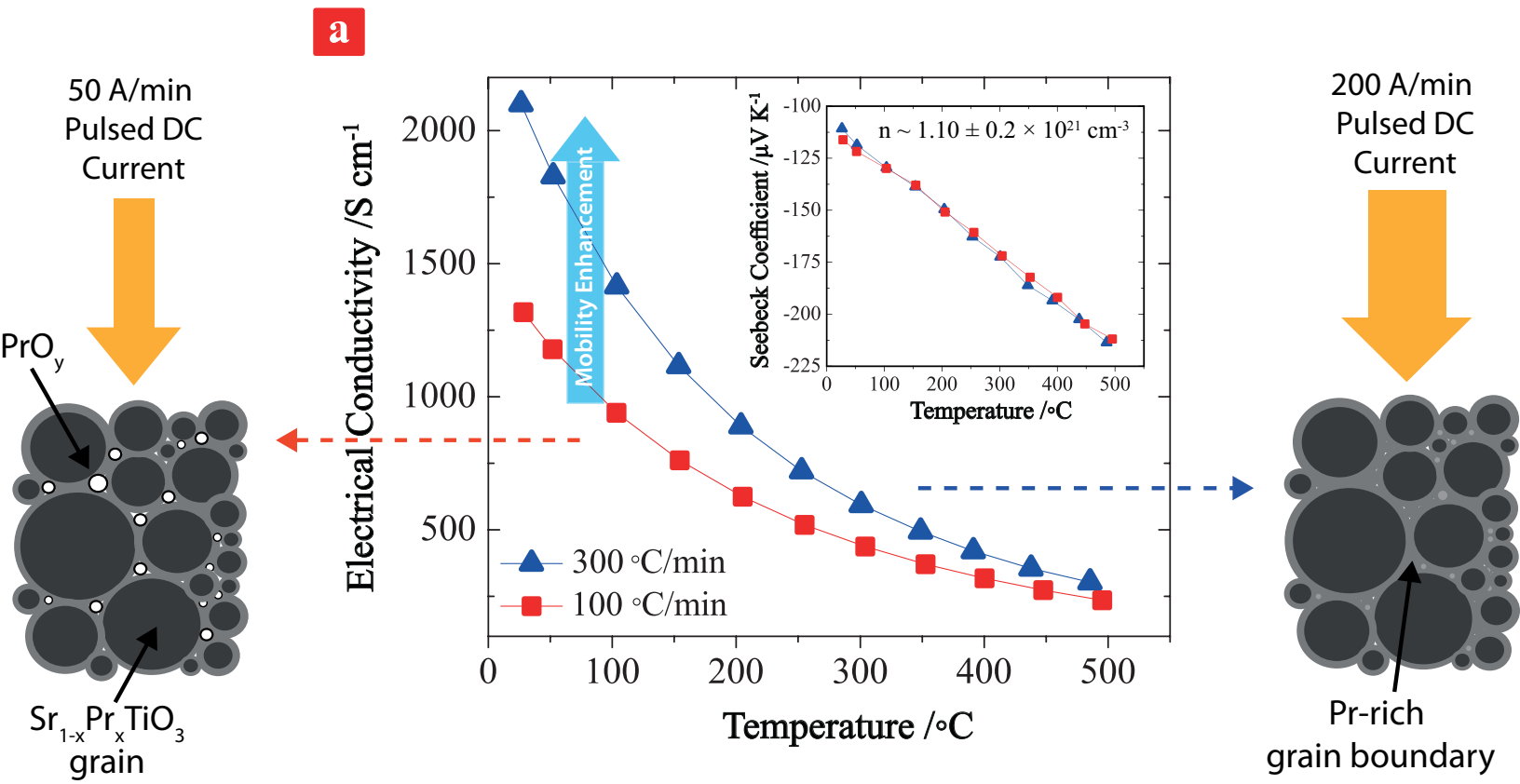

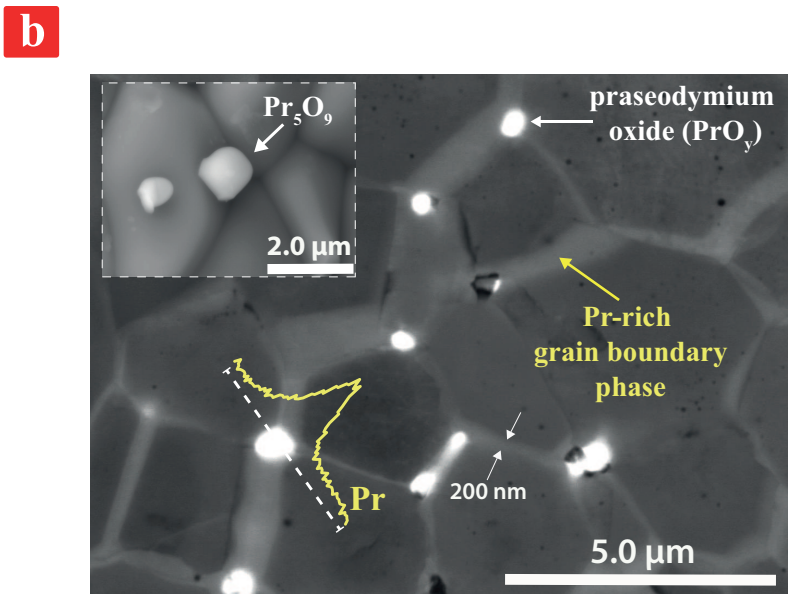

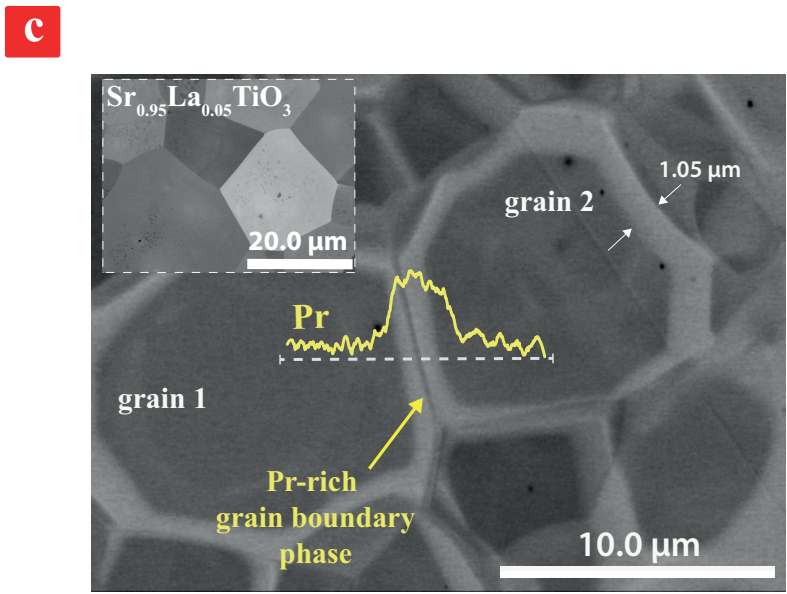

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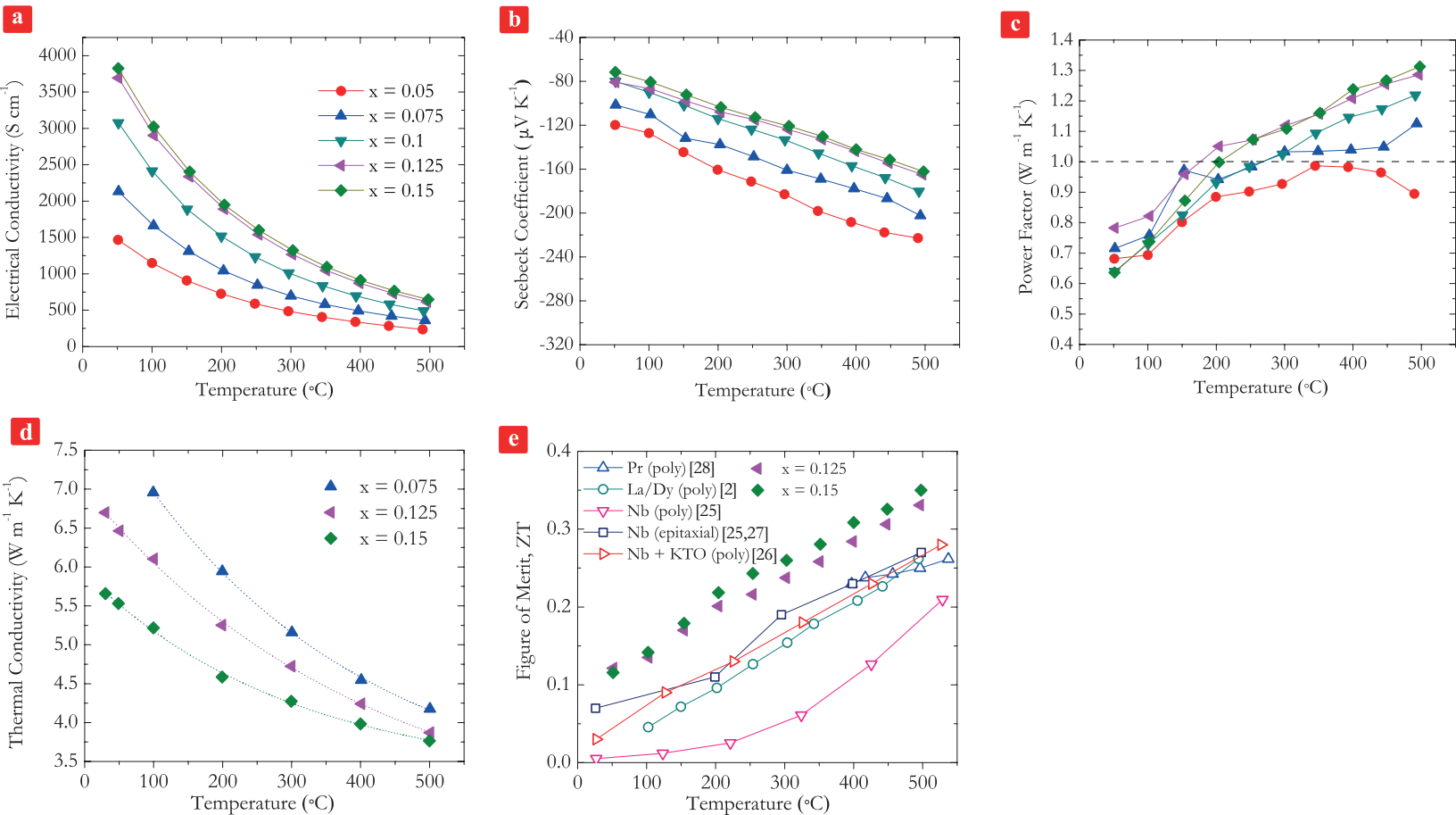

Excel Spreadsheet- Table of Materials/Equipment

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Name of Material	Company	Catalog Number
$SrCO_3$ Powder, 99.9%	Sigma Aldrich	472018
TiO_2 Nanopowder, 99.5%	Sigma Aldrich	718467
Pr_2O_3 Sintered Lumps, 99.9%	Alfa Aesar	35663

Name of Equipment		
Spark Plasma Sintering	Dr. Sinter Lab	SPS-515S
Resistivity/Seebeck Coefficient Measurement System	Ulvac-Riko	ZEM-2
Laser Flash Thermal Diffusivity Measurement System	Netzsch	LFA-457 Microflash
Differential Scanning Calorimetry (DSC) System	Netzsch	404C Pegasus
Physical Property Measurement system (PPMS)	Quantum Design	
Field Emission Scanning Electron Microscope (FE-SEM)	Hitachi	SU-6600
Energyy-dispersive X-ray Spectroscopy (EDS)	Oxford Instruments	
X-ray Diffractometer	Rigaku	Ultima IV
Bench-top Sputter Coater	Denton Vacuum	Desk II
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CLEMSON
PHYSICS AND ASTRONOMY

February 21, 2015

Journal of Visualized Experiments

Dear Editor:

We received the editorial and reviewers' comments on the manuscript JoVE52869 entitled "*Synthesis of Non-uniformly Pr-doped $SrTiO_3$ Ceramics and Their Thermoelectric Properties*" by Arash Mehdizadeh Dehkordi, Sriparna Bhattacharya, Taghi Darroudi, Husam N. Alshareef and Terry M. Tritt. We would like to express our appreciation for your time and efforts spent on handling our manuscript. We have revised and improved the manuscript according to the comments. Detailed response to the comments and the changes made in the manuscript are included at the end of this letter.

If you have any further questions or if any of our coauthors or us, may provide any additional information, please do not hesitate to contact us. Thank you for considering this manuscript for publication in the *Journal of Visualized Experiments*.

Sincerely yours,

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The manuscript has been revised and improved according to the comments. The changes made in the revised manuscript are included under the Response and Change sections below and are highlighted in the manuscripts using "Track-Changes" function of Microsoft Word. We believe that the critique have greatly improved the quality and clarity of the manuscript. Our responses to these comments are as follows:

Science Editor:

Comment #1: Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues. The JoVE editor will not copy-edit your manuscript and any errors in the submitted revision may be present in the published version.
Response: The manuscript has been proofread.
Comment #2: Please add more details to your protocol steps. Please ensure you answer the "how" question, i.e., how is the step performed? Alternatively, add references to published material specifying how to perform the protocol action.
Response: Additional information along with the reference for detailed operation was added to the steps of the protocol to answer the "how" questions.
Comment #3: 1.12: Should the pellet be ground after this second calcination process before 1.13?
Response and Change: Thank you for pointing this out. This intermediate grinding was added as an extra step.
Comment #4: 2.10: Followed by what of the current?
Response and Change: This sentence was rephrased.
Comment #5: 3.3: How is the pellet cut? Also, please indicate in which steps each kind of cut piece is used. If the steps are not included in the protocol, please give citations for the analysis.
Response and Change: The pellet is cut using a diamond saw. This information was added to the description of this step (3.3).
Comment #6: 3.4.1: Please provide a reference on how to perform the DSC. Also, please add the experimental parameters: how much of the samples were used, how long, etc.
Response and Change: The reference of DSC and the details of the measurement parameters were added to the manuscript.
Comment #7: 3.6: Please provide a reference on how to operate the gold sputtering unit. How are the tiny holes cut?
Response and Change: The reference of DSC and the details of the measurement parameters were added to the manuscript.
Comment #8: Please revise the highlighting of the protocol text for filming. Only 2.75 pages of highlighted protocol text is permissible and there are currently 3.25 pages. Please include all relevant details that are required to perform the step in the highlighting. For example: If step 2.5 is highlighted for filming and the details of how to perform the step are given in steps 2.5.1 and 2.5.2, then the sub-steps where the details are provided must be highlighted. The Protocol is >3 pages highlighted. The authors could possibly unhighlight parts of section 3, which appear to be standard techniques without much stepwise detail (like 3.7).
Response and Change: The parts which are not of considered a critical step in the filming were unhighlighted according to editor's comment.
Comment #9: JoVE cannot publish manuscripts containing commercial language. This includes trademark symbols (™), registered symbols (®), and company names before an instrument or

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reagent. Please remove all commercial language from your manuscript and use generic terms instead. All commercial products should be sufficiently referenced in the Table of Materials and Reagents. There is unnecessary branding in 1.6 and 2.4 (Carver) and in 3.2.1 (MicroFlash).
Response and Change: Commercial language including the names of the suppliers of the equipment was removed from the manuscript.
Comment #10: Overall, the discussion is more results than method oriented. The discussion needs to focus on the methods in terms of the 5 discussion requirements. Which steps are critical? Are there any modifications or troubleshooting that typically occurs? How are these methods superior to the alternatives? Please discuss the limitations and critical steps of the technique. What are some future applications of the technique? Simply stating "this work may open new horizons and opportunities to other properties and applications" is not very informative.
Response and Change: The important step(s) were highlighted throughout the protocol. The future opportunities of this synthesis method were clarified. The key differentiating the synthesis strategy described in this protocol from previous reports in the literature were highlighted in the discussion.
Comment #11: JoVE reference format requires that DOIs are included, when available, for all references listed in the article. This is helpful for readers to locate the included references and obtain more information. Please note that often DOIs are not listed with PubMed abstracts and as such, may not be properly included when citing directly from PubMed. In these cases, please manually include DOIs in reference information.
Response and Change: The DOIs of the references which were available were included in the reference list. We'd appreciate if the JoVE template can be modified to include the DOIs for future publications.

Reviewer #1:

Comment #1: Line 70 Reference is not defined.
Response: The reference to room-temperature electron mobility of $SrTiO_3$ had already been cited. It seems that Microsoft Word cross-referencing had a problem in updating the reference number. This issue was resolved.
Comment #2: Line 92 Reference is not defined.
Response and Change: Reference 12 has been cited for "spark plasma sintering technique".
Comment #3: Line 351 Reference is not defined.
Response and Change: Reference 13 has been cited for the results reported in Line 351.
Comment #4: Figures 2(b) and 2(c) are missing.
Response: Figures 2(b) and 2(c) have already been included in the Fig. 2.eps file uploaded before. It seems like the online pdf compilation system somehow did not incorporate the image.
Comment #5: Y-axis unit of Fig. 3(b) should be microV K^{-1} not mV K^{-1}.
Response and Change: Fig. 3 (b) was modified. It seems that the "mu" font had been change during file conversion.
Comment #6: Line 352-353 The authors mention that … whole temperature range over all previously reported maximum values were achieved …. However, no reference is cited.
Response: We thank the review for his/her comment. However, since the reported values were higher than reported in "all" previous publications we believe that the citations of selected

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previous reports might be unnecessary. However, Fig. 3 compares the results to some of the highest values reported in the literature. The references are included in the caption.

Reviewer #2:

Comment #1: Line 114: Researchers generally use the powder of Pr_2O_3 for synthesis. So the authors should shortly explain why the Pr_2O_3 sintered lump was used in the manuscript.
Response: We thank the reviewer for his/her comment. However, to the best of our knowledge researchers use both forms of Pr_2O_3. Alfa Aesar only supplies Pr_2O_3 in "sintered-lump" form which was chosen due to its competitive price comparing to the Pr_2O_3 supplied by Sigma-Aldrich. Nevertheless, our recent publication (Dehkordi *et al.*, J. Appl. Phys. **117** (2015) 055102) shows that the thermoelectric properties following the synthesis protocol presented in the manuscript is independent of the choice of Pr doping source.

Reviewer #3:

Comment #1: Line 70: Give references to the low carrier mobility of single crystals.
Response and Change: The reference to room-temperature electron mobility of $SrTiO_3$ had already been cited. It seems that Microsoft Word cross-referencing had a problem in updating the reference number. This issue was resolved.
Comment #2: Line 33-34: Power factor is already a defined term in thermoelectrics. The authors should change the phrase. "We herein define the numerator as the power
factor..."
Response: Traditionally, the thermoelectric power factor is defined in the Z context (not ZT) as $\sigma\alpha^2$ where σ is the electrical conductivity, and α the Seebeck coefficient. Researchers still generally define the power factor this way. However, here we define the power factor as $\sigma\alpha^2T$. Not only this definition portrays the actual temperature dependence of the electronic properties incorporated in ZT calculation but it also gives the SI SI of W/m-K similar to that of thermal conductivity.
Comment #3: Line 92: provide references to the conventional sintering.
Response and Change: Reference to "conventional sintering" had already been cited. It seems that the Microsoft Word cross-referencing had a problem in updating the reference number. This issue was resolved.
Comment #4: Line 118 and 120: "Weighted" powder should be "weighed" powder.
Response and Change: Thank you for pointing this out. The typo was fixed.
Comment #5: Line 123-124: 1.4) the step is not clearly understood. How does mixing of TiO_2 powder cause reduction of volume? Do the mixing process involve manual mixing or using any particular mixing instrument?
Response: The mixing can be done either manually or with a commercial tabulator/mixer. Since the TiO_2 is a nanopowder mixing help locally cold-pressing the powder to reduce the overall volume of the portion used so it can be fitted in the stainless steel die. This part was removed to avoid confusing the reader.
Comment #6: Line 131: "green body" is an unscientific language. Replace it with a more appropriate noun.

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Response: “Green body” is the technical term used primarily by ceramist for unsintered or unfired ceramics, which has been used extensively in the journal publications as well as the encyclopedia of advanced materials.

Comment #7: Line 138-141: 1.9) Define calcination first and then use the term. the phrase "let it reside.." is inappropriate in scientific papers. Replace it with clear words like "kept it at the elevated temperature.."

Response and Change: Calcination is a known technical term used by researchers in ceramics sciences and processing referring to the thermal treatment (firing) step in the solid-state reaction synthesis of ceramics. We do not believe this term needs to be defined here. The text was modified according to the reviewer’s comment on “let it reside…”.

Comment #8: Line 144: Has turbulator been used before during mixing the powders? If yes, mention.

Response and Change: Yes. The use of turbulator/mixer was added to step 1.4.

Comment #9: Line 267-271: The step describing the use of scotch-tape is not clear. The author should elaborate on this point for clear understanding to the general readers.

Response and Change: This step was clarified to explain the use of scotch tape as a stencil for the gold sputtering of the contacts.

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