2011

Thermoelectric oxides for waste heat recovery

Jayakanth Ravichandran

Jayakanth Ravichandran
Applied Science and Technology Graduate Program
University of California, Berkeley
Advisor: Prof. Ramamoorthy Ramesh, MSE/Physics

Final Report for Link Energy Fellowships:

Title: Thermoelectric oxides for waste heat recovery

Introduction:

Among various solid-state energy conversion methods, thermoelectricity deals with direct inter-conversion of thermal and electrical energy. The efficiency of a thermoelectric heat engine is related to a material dependent figure of merit, Z, given by $S^2\sigma/\kappa$, where S is the thermopower or Seebeck coefficient, σ and κ are the electrical and thermal conductivities (lattice and electronic), respectively. In conventional thermoelectric materials such as semiconductors, the density of states, chemical potential and the scattering mechanism governs electrical conductivity and thermopower. Due to this coupling between thermopower, electrical conductivity and electronic component of thermal conductivity, achieving high Z has been a challenging task. There are several proposals and/or demonstrations to design high efficiency thermoelectric materials such as "electron crystal, phonon glass" paradigm, [1] band engineering, [2] quantum confinement, [3] electron filtering [4] etc. The decoupling of lattice component of thermal conductivity from other parameters has been a very successful means to enhance the figure of merit, but further decoupling of parameters like electrical conductivity and thermopower is necessary to achieve high efficiency thermoelectric materials. From the technological perspective, it is essential to design highly stable, cheap and abundant materials with good efficiency for thermoelectric power generation. Complex oxides are an interesting class of materials, which provides a chemically tunable platform to realize a wide range of physical phenomena such as high temperature superconductivity (cuprates), ferroelectricity (titanates, ferrites), magnetism (manganites, cobaltates) etc. Due to this versatility, they can cater to both the scientific questions on thermoelectricity besides providing useful materials for technological applications. The aim of our research during the fellowship was to understand the nature of thermoelectricity in complex oxides and tailor these materials to show enhanced thermoelectric properties using existing or new physical principles discussed earlier.

The specific goals of my research was two fold:

(1) Understand the cross coupling between thermopower and electrical conductivity in complex oxides and identify the possibilities of decoupling and simultaneously increasing both properties with tunable material parameters.
(2) Explore the limits of phonon scattering at the interfaces of the oxide surfaces, particularly in the form of superlattices and use it to enhance the thermoelectric response in their doped analogues.

Research highlights:

Doped strontium titanate is one of the best n-type thermoelectric oxides. [5] Despite several investigations on the bulk form this material, a deeper understanding of the effect of different defects on electrical and thermal transport properties is still lacking. A thorough knowledge of the nature and role of defects in tuning the material properties is essential to evaluate the utility of band engineering in enhancing thermoelectric properties of this material. We demonstrated that thermal conductivity is a key parameter to evaluate the crystalline quality of $SrTiO_3$ films synthesized by different techniques. [iv] We have explored double doping (cationic doping and oxygen vacancy doping) as a means to enhance the thermoelectric power factor, [vii] and also studied the effect of each dopant on tuning the effective mass, which is one of the important quantity determining thermoelectric properties. [vi] We have investigated the favorable defect formation processes over the whole thermodynamic phase space for $SrTiO_3$ and have correlated with experimental observations. [ii] These investigations have provided a deep understanding of how electrical properties in $SrTiO_3$ can be tailored by controlling defects. Following on the electron transport studies, we explored strongly correlated thermoelectric material such as cobaltate. Particularly, we were interested in the relevance of Hicks-Dresselhaus proposal [3] of enhanced power factor for quantum-confined structures. In this regard, we studied thickness dependent thermoelectric properties of $Bi_2Sr_2Co_2O_y$ and found that in the ultra-thin limit of strongly correlated thermoelectrics, thermopower and electrical conductivity are uncoupled. [iii] Thus, strongly correlated materials provide an alternate dimension to complex oxide thermoelectrics.

Finally, we are studying the limits of interface phonon scattering of perovskite oxides such as $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$. Given that the doped analogues of these materials are good thermoelectric materials, it is judicious to identify the nature of phonon scattering in the superlattice structures of these materials. We find that the superlattices of $CaTiO_3/SrTiO_3$ and $BaTiO_3/SrTiO_3$ show the theoretically predicted thermal conductivity minimum as a function of superlattice interface density. This is a clear demonstration of the presence of coherent wave effect in terms of a macroscopic transport quantity such as thermal conductivity. [i] What are the direct consequences of the observation of such an effect? From the classical diffusive picture, the limits of thermal transport are very obvious and the alloy and amorphous limits are set using this knowledge. In the case of coherent wave regime, such limits could be breached and observation of phenomena, which don't conform to the diffusive framework, is also possible. Two examples of applications of this effect lie in (a) phonon localization and (b) phonon optics. Particularly, realization of phonon localization [6] is very relevant to thermoelectric applications. In the particular case, we propose "random superlattices" where the period thickness of the superlattice is randomized to create the necessary disorder to achieve broadband phonon localization.

This knowledge gives us the confidence to pursue complex oxides as a route to high efficiency thermoelectric materials both from the electron and phonon transport perspectives. I believe complex oxides will have a substantial role in the development of high temperature thermoelectric power generation based applications in the future.

Jayakanth Ravichandran
Applied Science and Technology Graduate Program
University of California, Berkeley
Advisor: Prof. Ramamoorthy Ramesh, MSE/Physics

Relevant publications:

i. **J. Ravichandran*,** A. K. Yadav*, R. Cheaito*, P. B. Rossen, A. Soukiassian, S. J. Suresha, J. C. Duda, B. M. Foley, C-H. Lee, Y. Zhu, A. W. Lichtenberger, J. E. Moore, D. A. Muller, D. G. Schlom, P. E. Hopkins, A. Majumdar, R. Ramesh and M. A. Zurbuchen, "Crossover from incoherent to coherent phonon scattering in epitaxial oxide superlattices", submitted to *Science*.

ii. E. Ertekin, V. Srinivasan, **J. Ravichandran**, P. B. Rossen, W. Siemons, A. Majumdar, R. Ramesh and J. Grossman, "Interplay between intrinsic defects, doping and free carriers in perovskite thin films", *Physical Review B,* **85,** 195460 (2012).

iii. **J. Ravichandran,** A. K. Yadav, W. Siemons, M. A. McGuire, V. M. Wu, A. Majumdar and R. Ramesh, "Size effects on thermoelectricity in a strong correlated electron system", *Physical Review B,* **85,** 085112 (2012).

iv. D-W. Oh, **J. Ravichandran,** C-W. Liang, W. Siemons, B. Jalan, C. M. Brooks, M. Huijben, D. G. Schlom, S. Stemmer, L. W. Martin, A. Majumdar, R. Ramesh and D. G. Cahill, "Thermal conductivity as a metric for the crystalline quality of $SrTiO_3$ epitaxial layers", *Applied Physics Letters,* **98,** 221904 (2011).

v. **J. Ravichandran,** J. T. Kardel, M. L. Scullin, J.-H. Bahk, H. Heijmerikx, J. E. Bowers and A. Majumdar, "An apparatus for simultaneous measurement of electrical conductivity and thermopower of thin films in the temperature range of 300-750 K", *Review of Scientific Instruments,* **82,** 015018 (2011).

vi. **J. Ravichandran,** W. Siemons, M. L. Scullin, S. Mukerjee, M. Huijben, J. E. Moore, A. Majumdar and R. Ramesh, "Tuning the electronic effective mass in double-doped $SrTiO_3$", *Physical Review B,* **83,** 035101 (2011).

vii. **J. Ravichandran,** W. Siemons, D-W. Oh, J. T. Kardel, A. Chari, H. Heijmerikx, M. L. Scullin, A. Majumdar, R. Ramesh and D. G. Cahill, "High temperature thermoelectric response of double-doped $SrTiO_3$ epitaxial films", *Physical Review B*, **82,** 165126 (2010).

viii. **J. Ravichandran,** W. Siemons, H. Heijmerikx, M. Huijben, A. Majumdar and R. Ramesh, "An epitaxial transparent conducting perovskite oxide: double-doped $SrTiO_3$", *Chemistry of Materials*, **22,** 3983 (2010).

References:

[1] Slack, G. A., *CRC Handbook of Thermoelectrics*, ed. DM Rowe, pp. 407– 40. Boca Raton, FL: CRC Press (1995).
[2] J. P. Heremans et. al. *Science,* **321**, 554 (2008).
[3] L. D. Hicks and M. S. Dresselhaus, *Phys. Rev. B* **47**, 12727 (1993).
[4] D. Vashaee and A. Shakouri, *Phys. Rev. Lett.* **92,** 106103 (2004).
[5] T. Okuda et. al. *Phys. Rev. B* **63,** 113104 (2001).

Jayakanth Ravichandran
Applied Science and Technology Graduate Program
University of California, Berkeley
Advisor: Prof. Ramamoorthy Ramesh, MSE/Physics

---

[6] P. G. Murphy and J. E. Moore, *Phys. Rev. B* **76,** 155313 (2007).

Note on discretionary funds:

The discretionary funding were spent on travel to conferences such as APS, MRS and a visit to the collaborator, Prof. Patrick Hopkins' lab for performing part of the thermal conductivity measurements. A sum of money was spent on buying computing software and hardware such as laptop.

Impact of the fellowship:

The fellowship had a significantly positive impact both during and after the graduate study. The fellowship provided the much-needed vigor to pursue energy research seriously and also a significant financial flexibility to pursue challenging problems in oxide thermoelectrics. Due to the support of the fellowship, my advisor was able to divert a portion of the funding towards research expenses instead of spending it on my stipend and travel. Currently, I am pursuing a post-doctoral research position with Prof. Philip Kim of the Physics department at Columbia University. Due to the encouragement of the Link fellowship, I am pursuing research on superconductors, which have a significant role in the shaping the future of the energy landscape. In the long term, I plan to pursue an academic career in the university to explore energy related problems. I believe that Link Energy fellowship provides an ideal platform and encouragement for young graduate students to pursue a research career focused on energy.