Thermoelectric Materials with Potential High Power Factors for Electricity Generation

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The thermoelectric figure of merit ZT of materials limits the performance of a thermoelectric power generator. To date, the main gains from the worldwide effort in either engineered bulk materials or low-dimensional systems have been mostly based on the strategies of reducing the thermal conductivity. We explore several bulk thermoelectric materials that have respectable mechanical strength and chemical stability at elevated temperatures for potential power generation. Our strategy is to first explore the avenue of significantly increasing the power factor (PF), then the avenue of lowering thermal conductivity, perhaps by nanocompositing. We examine the layered cobaltates with sharp resonant peaks in the electronic density of states near the Fermi energy level due to strong electron correlation. We suggest that electron correlation may be used as a new tuning parameter to significantly increase the PF. We also report that a substantial increase (over 30%) in PF can be achieved in filled skutterudites (such as p-type $CeFe_4Sb_{12}$) through nonequilibrium synthesis by rapid conversion of the amorphous materials made by the melt spinning to single-phase crystalline materials under pressure. This process, in conjunction with the rattling to lower the lattice thermal conductivity, could further enhance the ZT values of the filled skutterudites.

Key words: Thermoelectrics, filled skutterudite, cobaltate, melt spinning

INTRODUCTION

Ideal thermoelectric materials should have good electrical properties [high power factor (PF) $S^2\sigma$], but poor thermal conductivity. However, the electrical and thermal properties of a material are determined by the same crystal and electronic structure. Usually, they cannot be controlled independently. The challenge is to find ways to decouple the electrical and thermal properties. Since the early 1990s, two approaches have been developed (mostly along different directions) in the research for thermoelectric materials with a ZT value above unity: one uses engineered bulk materials,[1,2] whereas the other employs low-dimensional materials.[3–5] In the first approach, complex crystal structures are designed and synthesized to have the properties of an electron crystal/phonon glass, that is, the electrical properties of crystalline materials, and the thermal properties of amorphous or glass-like materials.[6] In the second approach, low-dimensional materials, such as superlattices[4] and quantum dots,[5] are designed and synthesized to increase the electron density of states (DOS) at the Fermi level by quantum confinement of electrons,[3] and boundary scattering of phonons to reduce the thermal conductivity. Quantum-dot superlattices (QDSLs) in the PbTe/PbTeSe systems have demonstrated ZT values of up to 2.4, twice those of classic bulk materials.[5] More recently, the two approaches seem to be converging, as the new bulk thermoelectric materials are host materials containing nanoscale inclusions; for example, Hsu et al.[7] reported nanoscale-inclusion-containing bulk $AgPb_mSbTe_{2+m}$ with a ZT of 2.1 at 527°C. Although high ZT values were reported in QDSL materials, it is rather difficult to use them in large-scale energy conversion because of their limited heat transfer and

high cost. Bulk materials with high ZT value are ideal for moderate to high-temperature applications, such as waste-heat recovery or solar-energy harvesting. Other important considerations for power generation at elevated temperature are the chemical stability and thermal-mechanical strength, e.g., thermal shock parameter, as well as some environmental issues of the toxic chemical, such as lead. Oxides and filled skutterudites appear to be ideal in large-scale power generation if their ZT values can be further enhanced.

To date, the main gains from the worldwide effort in increasing the ZT value in either engineered bulk materials or low-dimensional systems have been based on the strategies of reducing the thermal conductivity,[8] either by increasing the effect of "rattlers" in the case of skutterudites-like materials[9] or by increasing the presence of interfaces which scatter phonons more effectively than electrons.[8] To achieve remarkably higher ZT values, it may not be enough just to decrease the thermal conductivity. A significant increase in the PF is also necessary.[10]

Our approaches are to explore both avenues, increasing the PF and reducing the thermal conductivity. The strategy is to first explore the avenue of significantly increasing the PF, then the avenue of lowering thermal conductivity, perhaps by a nanocomposite approach. In the first part of this article, we examine the layered cobaltates and show that strong electron correlation can induce a sharp resonant peak in the electronic DOS near the Fermi energy level. We suggest that electron correlation may be used as a new tuning parameter to significantly increase the PF. In the second part, we report that a substantial increase in PF can be achieved in filled skutterudites (such as p-type $CeFe_4Sb_{12}$) through nonequilibrium synthesis by rapid conversion of the amorphous materials made by the melt spinning to single-phase crystalline pellets at high pressure under a few minutes. This rapid conversion process is an economical and scalable process for developing high-performance thermoelectric materials.

LAYERED COBALTATES

High thermoelectric power ($S \sim 100$ μV/K at room temperature) was discovered in sodium cobaltates ($Na_{0.5}CoO_2$) showing metallic behavior in 1997 by Terasaki et al.[11] Inspired by this discovery, there is now a worldwide search for potential thermoelectric oxides. Current research is mostly focused on Co-based layered oxides, such as Na_xCoO_2 and $Ca_3Co_4O_9$, which possess the highest ZT values among oxides, and are chemically stable with the potential to be used in thermoelectric power generation at temperatures above 800 K.[12,13] Layered cobaltates feature alternatively stacked conducting CoO_2 blocks, where Co ions define a triangular lattice, and insulating blocks with incoherent layer boundaries, producing highly anisotropic transport properties along their crystallographic directions. There are two major groups of layered cobaltates: (1) intercalated, such as Na_xCoO_2, where the Na ions are sandwiched between CoO_2 layers[11]; and (2) misfit, such as $Ca_3Co_4O_9$, consisting of alternating layers of the triple rock-salt-type $[Ca_2CoO_3]$ subsystem and the single $[CoO_2]$ subsystem.[13,14] Structure-wise, they may be viewed as self-assembled misfit superlattices. The incoherent boundary interface results in strong phonon scattering, while charge carrier transport is unhindered along the conducting (CoO_2) plane.

Unlike the electronic structure of a semiconductor, where only charge is relevant, the electronic structure of cobaltates is influenced not only by charge, but also by the spin, lattice, and orbital degrees of freedom, leading to giant responses to small perturbations.[15] This is the result of competing order parameters and strong electronic correlations. It is our view that a new paradigm is emerging that potentially offers a revolutionary approach to significantly increase the PF by manipulating the electronic correlations. This new approach is conceptually different from the conventional one used for the last 50 years, which is based on the band theory of semiconductors. In the conventional approach, the shape of single-electron DOS and the position of E_F in a semiconductor are tuned by adjusting one or more of the parameters controlling the carrier concentration, mobility, number of carrier pockets, and energy-filtering process. In semiconductors, the carrier concentration usually changes as a function of temperature, whereas in the correlated oxides, there is usually no change in the carrier concentration with temperature. The change in the electronic structure is accompanied by a shift in electronic spectral weight, which can be further controlled by tuning the electronic correlations. Recently, we demonstrated in cobaltates that electronic correlations can dramatically change the electronic structure of the system,[16] and that this may contribute to an orders-of-magnitude enhancement of thermoelectric power.[12]

Figure 1a shows a large shift in the quasiparticle spectral weight as temperature increases in a cobaltate determined by angle-resolved photoemission spectroscopy (ARPES). Figure 1b shows the temperature dependence of the in-plane (along Co-O layer) and out-of-plane electrical resistivity. A crossover from low-temperature metallic-like to high-temperature insulator-like behavior is observed along the c-axis, although the in-plane transport maintains a metallic-like behavior. This crossover is reflected in the electronic structure by a very narrow quasiparticle band ($\hbar\omega_c \sim 20$ meV) at low temperature, which disappears at high temperature. This crossover is interpreted as a shift from three-dimensional (3D) coherent quasiparticle excitations at low temperature to two-dimensional (2D) incoherent excitations at high temperatures. Strong
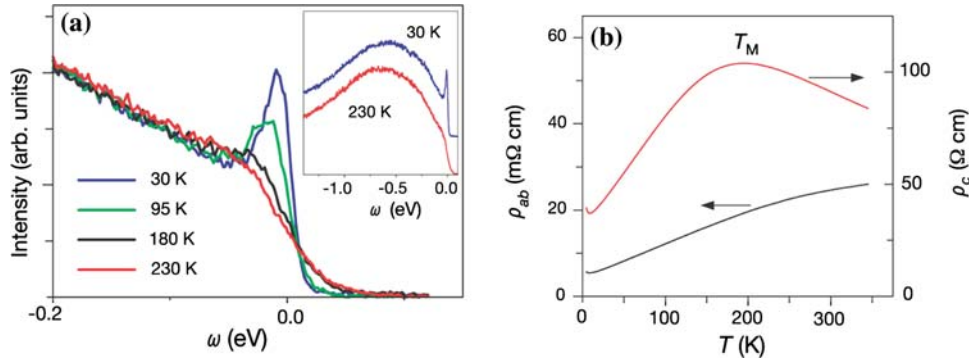
Fig. 1. Corresponding ARPES and transport data of $(Bi_{0.5}Pb_{0.5})_2Ba_3Co_2O_y$ single crystals. Similar behavior was also observed in Na_xCoO_2 single crystals. (a) The changes in energy distribution curves with temperature. The inset shows the wide-range energy distribution curves. (b) In-plane and out-of-plane resistivities measured on a sample from the same batch.[16]

electronic correlations that result in the thermal destruction of the Fermi liquid occur at the crossover temperature $T_M \sim 200$ K.

The observation of a crossover from coherent quasiparticle excitations at low temperature to incoherent excitation at high temperature in cobaltates is consistent with the prediction by the dynamic mean-field theory for strongly correlated electron systems. We recently argued that an extremely narrow quasiparticle bandwidth, or resonant peak, observed in cobaltates drastically changes the dynamics of electron transport, suggesting the thermoelectric power S of cobaltates scales with $h\omega_c$ ($S \propto kT/h\omega_c \propto T/T_M$) at $T < T_M$.[12] Above T_M, the dominant incoherent excitation leads to a weak temperature dependence in S. Such behavior is in striking contrast to that of a simple metal, where the characteristic energy scale of the carriers is determined by the Fermi level E_F (~ 1 eV), and S scales with E_F, that is $S \propto kT/E_F$. The E_F ($\sim 10,000$ K) in simple metals is now replaced by the $h\omega_c$ in cobaltates. A change in the energy scale of approximately two orders of magnitude may contribute to the large enhancement of the thermoelectric power in cobaltates ($S \sim 100$ μV/K) over the simple metals ($S \sim 1$ μV/K to 2 μV/K) at elevated temperatures, in addition to the spin entropy contribution in the cobaltate system.

Although there are additional interactions (e.g., spin) in cobaltates that can be used as tuning parameters for its DOS, electronic correlations appeared to be the most powerful one that determines the transport behavior of the correlated electronic materials. To change the electron correlation, there are two approaches: band-filling control and bandwidth control. Band-filling control involves introducing charge carriers (doping) by changing the electron filling level (d-band), for instance, alloying divalent ions (e.g., Sr^{2+} and Ca^{2+}) at the trivalent (e.g., La^{3+}) ions site in transition-metal oxides. Bandwidth control involves reducing the bandgap. Isoelectronic chemical doping (because of different ionic radii), epitaxial strain, and reducing dimensionality may be used to change either the on-site Coulomb repulsion U or bandwidth ω_c.

NONEQUILIBRIUM SYNTHESIS OF FILLED SKUTTERUDITES

The filled skutterudite antimonides are an excellent approximation of an ideal thermoelectric solid with the good electrical transport properties of a crystal but the poor thermal conduction of a glass, as first proposed by Slack.[6] The basic idea is to have semiconductors in which one of the atoms is weakly bound in a large atomic cage. Such an atom inside the cage "rattles" due to large local anharmonic vibrations, which drastically lowers the lattice thermal conductivity. In thermoelectric filled skutterudites (general formula RM_4X_{12}, where M is a transition metal, e.g., Fe or Co, and R is a rare-earth element, e.g., La, Ce[17]), the crystal structure is body-centered cubic with 34 atoms in the conventional unit cell consisting of square planar rings of four pnicogen atoms (X). The metal (M) atoms form a simple cubic sublattice and the R atoms are positioned in the two remaining holes (or cages) in the unit cell. It is generally believed that the rattling of the rare-earth ion is responsible for reducing the lattice thermal conductivity to a value within two or three times κ_{min}, while preserving the favorable electrical properties. κ_{min} is attained when the mean-free path of the heat-carrying phonons is comparable to the phonon wavelength and corresponds to the thermal conductivity of an amorphous solid with the same chemical composition. The estimated mean-free path of the heat-carrying phonons at room temperature is ~ 0.75 nm in filled skutterudites, which agrees well with the nearest-neighbor separation of the rattlers, 0.8 nm. In bulk materials, κ_{min} is the lower limit to the lattice thermal conductivity, although lower values have been seen for interfacial heat transfer.[6] In our view, significant progress of increasing the ZT value beyond equilibrium filling the atomic cages in the skutterudites must come from increasing the PF.

The electrical transport in the filled skutterudites is altered by the presence of the rattlers, essentially the chemical doping or the filling. Relative to the analogous unfilled compounds, the filled skutterudites exhibit larger effective masses, suggesting a

moderately heavy fermion ground state,[18] where electron correlation can play an important role, as in the case of cobaltates. We recently developed a new route of increasing the PF of the filled skutterudites using the nonequilibrium synthesis techniques with the encouraging result of achieving over 30% increase in the PF through the combined use of melt spinning and rapid conversion under pressure in p-type $CeFe_4Sb_{12}$.[19]

In filled skutterudites, such as $CeFe_4Sb_{12}$, the filling fraction limit of each impurity atom (e.g., the rare-earth element) in the host skutterudite structure is determined by many factors such as the charge state, the electronegativity, etc., of the filler.[20] Also, the filling fraction limit of an impurity is affected by the formation of secondary phases between the impurity and the host atoms. The secondary phases could be energetically close to or more favorable than the filled skutterudite phases, e.g., impurity phase of $FeSb_2$ in $CeFe_4Sb_{12}$. Under the equilibrium condition, the actual doping level obtained experimentally is driven by thermodynamics. Sales et al.[17] pointed out earlier that, while good overall electrical transport is maintained as indicated by the large values of ZT at elevated temperatures, the high carrier concentrations in the filled skutterudites are due mostly to the fraction of the rare-earth sites that remain empty in samples prepared using equilibrium synthesis. Hence, using the nonequilibrium synthesis process, particularly with high driving force, we could achieve a signifi-cant large deviation from the equilibrium filling fraction limit (or doping level) by the direct conversion of amorphous material into crystalline phase under pressure. By varying both intrinsic and extrinsic carrier concentration in the filled skutt-erudites, it is possible to get a higher value for ZT by simultaneously increasing the thermopower S and decreasing the lattice thermal conductivity $\kappa_{Lattice}$. This is because, in the nonequilibrium synthesis with high driving force (pressure), the filling fraction may be increased above the equilibrium level so that the decreased extrinsic carrier concentration could yield higher S, while the increased number of rattlers inside atomic cage could further reduce the $\kappa_{Lattice}$. It must be emphasized that the nonequilib-rium synthesis of direct and rapid converting the amorphous materials into the crystalline phase under pressure is fundamentally different from the conventional equilibrium synthesis with hot-press sintering, where the phase of filled skutterudites is formed by long-term sintering, and followed by the hot-press for densification, rather than providing an environment for chemical reaction.

Figure 2a shows a bag of ribbons collected after melt spinning of the ingot with the nominal com-position of $CeFe_4Sb_{12}$. Rapid solidification by the melt spinning produces ribbons of ~ 5 μm to 20 μm thick. X-ray diffraction and transmission electron microscopy studies of the powdered ribbon reveal that the majority of the materials in the ribbons are amorphous with a trace of nanocrystals embedded.
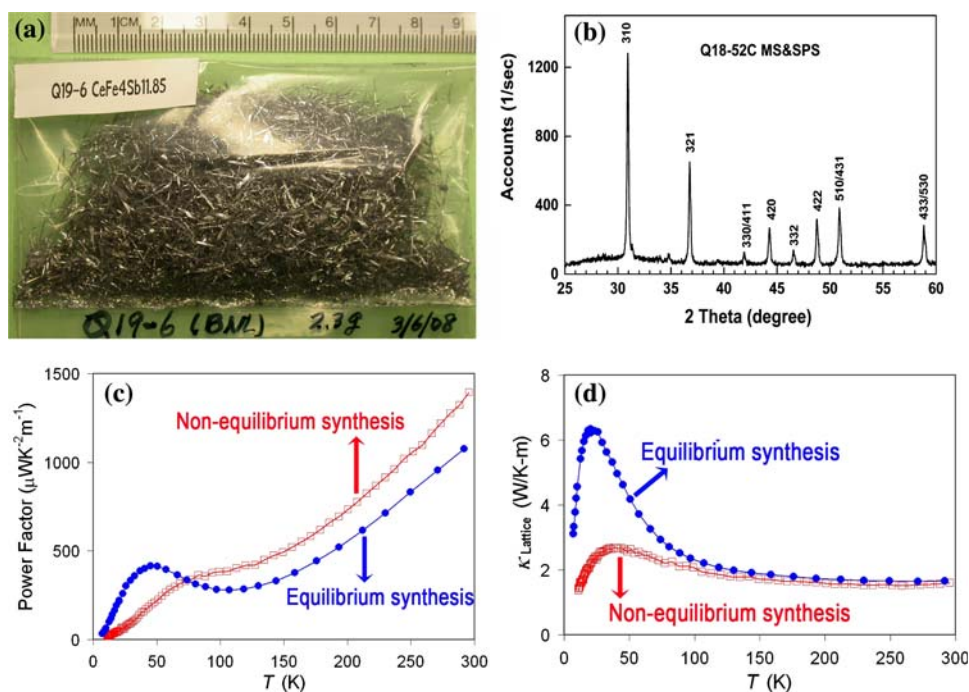

Fig. 2. (a) Melt-spun ribbons of $CeFe_4Sb_{12}$; (b) x-ray diffraction pattern of melt spun samples after 2 min of spark plasma synthesis showing complete conversion of the amorphous materials into single-phase $CeFe_4Sb_{12}$; (c) and (d) temperature dependence of the PF and lattice thermal conductivity of the nonequilibrium (MS + SPS) synthesized samples and that made by the conventional equilibrium synthesis.

The ribbons are packed and sintered in spark plasma sintering (SPS) or hot-press at around 600°C for as little as 2 min under a pressure of 60 kN. The resulting pellet is fully dense and of single-phase $CeFeSb_{12}$ as examined by the x-ray diffraction pattern shown in Fig. 2b. Figure 2c and d shows comparative plots of the temperature dependence of the PF and lattice thermal conductivity of the nonequilibrium (MS + SPS) processed samples and that made by the conventional equilibrium synthesis. At room temperature, the lattice thermal conductivity is comparable for both nonequilibrium and equilibrium synthesis, but significantly reduced for the nonequilibrium synthesized samples at low temperatures below 100 K, while more than a 30% increase in the PF was observed in the nonequilibrium synthesized samples above 100 K. The hump in the PF around 50 K for the equilibrium synthesized samples is presumably related to the tendency of the Ce $4f$ level to hybridization at low temperature, and is beyond the scope of this paper.

CONCLUSIONS

In summary, new directions for increasing the performance of thermoelectric materials are given here by examining the transport properties of cobaltates and nonequilibrium synthesized filled skutterudites. It is remarkable that the spectral function of cobaltates has all the characteristic features given by the DMFT for a doped Mott insulator. The extremely narrow quasiparticle band is shown to be the mechanism leading to the high thermoelectric power. It is also argued that the nonequilibrium synthesis has a great potential to enhance the thermoelectric property of complex materials, as we demonstrated in the case of p-type filled skutterudites $CeFe_4Sb_{12}$, where over 30% increase in the PF at room temperature was achieved, while lattice thermal conductivity was reduced at low temperature. Equally important is that this rapid conversion process is an economical and scalable process that provides the platform for developing high-performance thermoelectric materials.

ACKNOWLEDGEMENTS

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