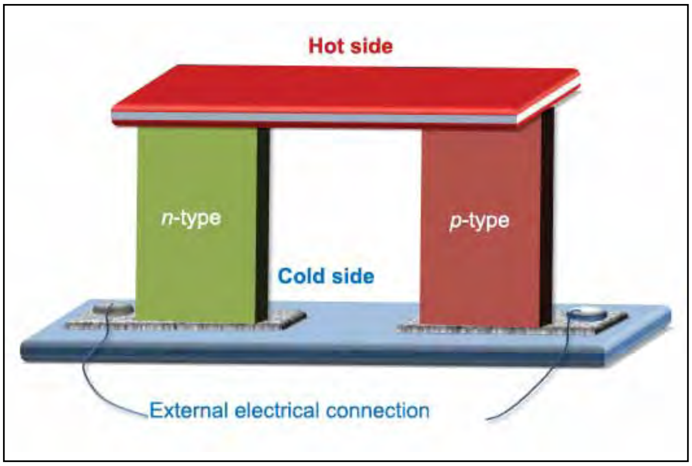

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Figure 1. Schematic of a thermoelectric module.

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High-temperature oxide thermoelectrics

Scott Misture and Doreen Edwards

Conversion of waste heat to electrical energy using oxide thermoelectric generators might revolutionize the efficient use of energy in the future.

Direct conversion between thermal and electrical energy using thermoelectric materials may revolutionize energy efficiency throughout modern society. Capturing waste heat and converting it directly to electrical energy using thermoelectric generators is one possibility, and the reverse possibility is high-efficiency active cooling via the Peltier effect.

The TE effect occurs when a solid is exposed to a temperature gradient, which drives the diffusion of charge carriers—either electrons or holes—along the temperature gradient. The Seebeck coefficient (*S*), sometimes called the thermoelectric power, is a material-specific measure of the resulting electrical potential. The Peltier effect describes how junctions of dissimilar materials can be heated or cooled depending on the direction of current flow.

Connecting *n*- and *p*-type legs as shown in Figure 1 creates a TE module. TE modules are adaptable to many configurations, including thin-film forms, requiring only that the temperature gradient be maintained across the module. A key advantage of TE technologies is scalability, applications that range from personal electronics to fixed power stations are envisioned.

A TE generator converts heat to electricity by the Seebeck effect when a voltage is created by a temperature difference across a solid. The overall efficiency of the device is captured by a dimensionless figure of merit (*ZT*), which depends on the materials' Seebeck coefficient, electrical conductivity (σ), thermal conductivity (k) and absolute temperature (T), according to

$$ZT = S^2\sigma T/k \qquad (1)$$

TE materials with $ZT \approx 1$ are considered high-performance materials with potential for commercial application. Values as high as $ZT \approx 2.5$ have been reported for nanostructured semiconductors near room temperature,[1–6] however a general goal general goal of the TE research community is to reach $ZT \approx 3$ for large-scale commercialization.

As with many technologies, the TE materials themselves limit the overall performance. The performance is linked to electrical and thermal conductivity. TE materials require minimal thermal transport and high electrical conductivity with a large Seebeck coefficient. These requirements lead to the common description of the ideal TE material behaving as an "electron-crystal but phonon-glass," where the electronic conductivity is large, as in a crystal, but the lattice thermal conductivity is small, as in an amorphous solid.

Nanoscale features, although largely crystalline, approach the glassy state in many respects.

Current understanding of phonon transport and electrical behavior points to the use of nanostructured "low-dimensional" solids, where 2D and even 1-D features may substantially increase *ZT* and decrease thermal conductivity. Notable progress has been made toward decreased lattice thermal conductivity via nanostructured composites, where phonon scattering at interfaces substantially decreases thermal conductivity. However, success in using quantum confinement of charge carriers in nanofeatures to increase *ZT* remains elusive.

Thus far, semiconducting materials have received the most attention, with materials like SiGe, PbTe and $Yb_{14}MnSb_{11}$ facilitating high *ZT* for *n*- and *p*-type TE elements. Extensive studies of bulk nanostructured solids clearly show that introducing nanoscale features into the solid is an effective means of decreasing the thermal conductivity and, thus, increasing *ZT*.

Because of the complex interplay between the electrical and thermal behaviors in TEs, other approaches have been used to probe their interrelationships. For example, the use of 2D superlattice structures has been demonstrated as a means of filtering the low-energy charge carriers and as a means of decreasing thermal transport, where both effects work together to increase *ZT*.[5,6]

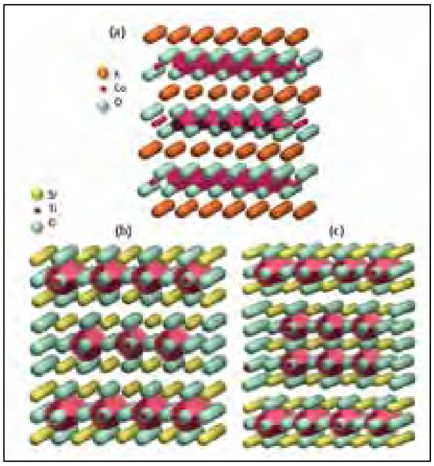
Useful anisotropic properties from hybrid unit-cell structures

Ceramic TEs may allow a jump to higher service temperature regimes because of their stability at high temperatures in oxidizing and corrosive environments. The rich crystal chemistry of oxides encourages strategies of multiscale nanostructuring by considering "hybrid" crystal structures that contain discrete structural blocks or layers. Of course, nanostructuring these hybrid materials or assembling them as highly oriented polycrystalline solids or as composites also is envisioned. The size scales span from the unit-cell to the microscale.

At the unit-cell level, oxide crystal structures offer many options as hybrid structure types, including layered 2D structures and 1-D tunnel structures. With feature sizes less than five nanometers, the crystallography may define structural features that support quantum confinement of charge carriers and disrupt or filter phonons, while remaining thermodynamically stable during high-temperature operation. For example, in the layered oxides, dopants might be used in specific structural layers. Likewise, there could be variations in layer thickness, interlayer strain and interfacial roughness to optimize *ZT*. Furthermore, 1-D and 2D structural features may facilitate decoupling of the electrical and thermal transport and offer the ability to exploit highly anisotropic properties.

At size scales larger than the unit-cell, nanoscale processing can help achieve desirable bulk structures, nanocomposites and superlattices, all of which remain largely unexplored in oxides. Functionally graded materials also are of interest, as are segmented *n*- or *p*-type legs that incorporate multiple TE materials to optimize efficiency along the entire temperature gradient.

Several recent reviews[1,5,6] demonstrate that many opportunities exist for the study of oxide TE materials. The layered or hybrid or "natural superlattice" crystalline materials (Figure 2) are the primary oxide TEs thus far discovered, but there are several complex 3D or reduced oxides that also show high *ZT*. Mindful of the controversy related to inaccurate estimates of *ZT*, generally *p*-type oxides reach *ZT* = 1, while the



(Credit: Misture.)

Figure 2. Layered thermoelectric structure types: (a) *p*-type $K_{0.5}CoO_2$ (idealized); and (b, c) two members of the Ruddlesden–Popper series, Sr_2TiO_4 and $Sr_3Ti_2O_7$. The red polyhedra represent TiO_6 units within the structure.

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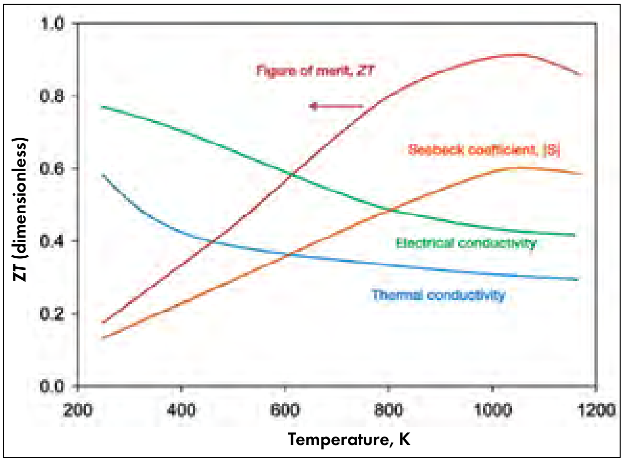

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Figure 3. Schematic of the temperature dependence of the thermal and electrical conductivities and Seebeck coefficient as well as the resulting *ZT*.

n-type reach only about half that value at high temperature.

To achieve higher-temperature operation, for example, T_{hot} greater than 1000°C, oxide materials provide several key advantages:

- High-temperature chemical stability in oxidizing environments;
- Stable microstructures or nanostructures at elevated temperature; and
- Unusually low thermal conductivity, as low as $k \approx 1$ watt per meter·kelvin at 1000°C, across planes in layered crystals at high temperatures.

Layered cobalt-based oxides are *p*-type conductors achieve $ZT > 1$ and achieve technologically relevant *ZT* values exceeding unity at temperatures up to 700°C. Example materials include A_xCoO_2 and $Ca_3Co_4O_9$. In contrast, the *n*-type analogs suffer from low TE efficiency, although very recent reports of high *ZT* in *n*-type TEs are promising. For example, the oxygen-deficient fluorite $Ga_{3-x}In_{5+x}Sn_2O_{16}$ has a *ZT* of approximately 0.3 at 1000 K, and the many variants of doped $SrTiO_3$ have *ZT* up to approximately 0.4 at 1000 K.

Another class of active materials is highly reduced oxide ferroelectrics. Coupled ferroelectric–thermoelectric materials with oxygen deficiency have shown high-TE power factors and nanoscale features, a result of oxygen vacancy clustering on the size scale of 5–10 nanometers. Examples include the tungsten bronze $Sr_xBa_{1-x}Nb_2O_{6-\delta}$ and the layered $Sr_2Nb_2O_7$.[2,7] Indeed, there have been recent reports (thus far not yet reproduced) of oxide superlattices offering remarkable properties, with $ZT = 2.4$ estimated for the conducting layer in a $SrTiO_3/SrTiO_3$:Nb superlattice.[1]

The subtleties of the atomic arrangements have an enormous impact on the electronic band structures and, therefore, on the thermopower in oxides. Recent work has shown that distortions of the TiO_6 octahedra in $SrO(SrTiO_3)_n$ Ruddlesden–Popper phases dominate the Seebeck coefficient.[1] Crystal field splitting resulting from octahedral distortions breaks the spin-orbital degeneracy of the three titanium t_{2g} orbitals at the bottom of the conduction band, decreasing the density of states, effective mass and Seebeck coefficient. Even slight distortion of the octahedra by a few degrees is sufficient to dramatically alter the Seebeck coefficient and *ZT*. For example, $SrO(SrTiO_3)_2$ with niobium doping and distorted octahedra has $ZT = 0.14$. Lanthanide doping, however, yields nearly perfect octahedra and $ZT = 0.24$. Furthermore, thermal expansion slightly decreases the octahedral distortions, thus improving the Seebeck coefficient at higher temperatures.

A primary advantage of the layered oxides is unusually low thermal conductivity normal to the layers and, in some cases, parallel to the layers. For example, highly textured polycrystalline specimens of the ferroelectric materials $Bi_4Ti_3O_{12}$ (Aurivillius structure) and $Sr_2Nb_2O_{10}$ ($Sr_nNb_nO_{3n+2}$ homologous series) have $k \approx 1$ watt per meter·kelvin through 1000°C across the layers, which is nearly constant with temperature. In the other two directions, thermal conductivity values are 1.5–2 watts per meter·kelvin, also largely invariant with temperature. Even the in-plane values are substantially lower than typical ceramics,[8] and the cross-plane values are competitive with the state-of-the-art semiconducting materials.[4,6]

The unusual temperature independence raises new questions about the thermal transport mechanisms in these complex oxide structures. When phonon scattering from defects is considered and the mean free path is estimated on the order of the interatomic spacing, the anisotropy in thermal conductivity is concluded to be attributable to phonon scattering because of the acoustic mismatch between layers with substantially different density and thickness.

Although the 2D nature of layered oxides may be exploited to decrease the thermal conductivity in an anisotropic fashion, the necessity to maintain the electrical performance along the temperature gradient must also be considered. Deliberate design of the atomic structures, nanostructures and microstructures therefore requires knowledge of the anisotropy in the electrical and thermal properties.

Thermoelectric devices

Overall device efficiency depends on optimum TE performance along the temperature gradient and matched properties of the *n*- and *p*-type legs, both of which are difficult to achieve. The thermal, thermoelectric and electrical properties are all functions of temperature, as shown schematically in Figure 3. The *ZT* values for oxide TEs may vary by a factor of 10 from room temperature to high temperature, with peak values generally at higher temperatures. In contrast to semiconductors, the thermal conductivity decreases with temperature, generally by a factor of two or more, and it is typical for the thermal conductivity of bulk materials to reach values as low as 1–2 watts per meter·kelvin at 800–1200°C.

Optimizing the device efficiency is possible using segmented TE materials along the temperature gradient or functionally graded materials that have properties optimized for maximum *ZT* along the temperature gradient. The overall TE device efficiency can be predicted, assuming matched *n*- and *p*-type legs and temperature-independent ZT values with a hot side temperature of 727 K (1000°C).[4] For a cold side of 300 K, an average $ZT \sim 1$ will yield 20-percent efficiency. Larger thermal gradients improve efficiency. Therefore, for a cold side of 100 K, 20-percent efficiency is achieved at $ZT \approx 0.8$. Unfortunately, the assumption of temperature-independent ZT is not generally realistic, as shown in Figure 3. Therefore, oxide TE researchers need to address the opportunities and challenges of segmented or graded TE materials.

Designs for full TE modules may prove rather straightforward compared with some existing energy conversion technologies. The TE module has no moving parts and by necessity has only one end operating at elevated temperature. There are challenges related to the stability of nanostructured materials, corrosion resistance, thermal expansion matching and electrode stability at the hot end, but these challenges appear to be manageable.

Outlook

Advances in oxide TEs, especially *n*-type materials, may establish new benchmarks for device efficiency in the high-temperature regime. TE researchers already are applying some of the knowledge gained in the study of semiconducting TEs to the oxides.

Fundamental questions remain concerning the impacts of 1-D and 2D nanostructures on Seebeck coefficient and thermal conductivity, and oxides likely will provide the best platform for future, studies in heterogeneous 2D crystals. Synthetic heterostructures also may provide new experimental insights, and, of course, computational methods will grow in importance to broaden the knowledge base.

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