

Mutagenesis of yeast followed by identification of strains unable to replicate RNA3 has shown that expression of several yeast genes is required for its replication. To date genes in three complementation groups, called mab-1, 2, and 3 (for maintenance of BMV functions), which presumably encode three different proteins, have been partially characterized (13). Because the mutant yeast are temperature sensitive, it is clear that these gene products are also required for normal cell growth. In the yeast cell, protein 1a stabilizes 2a, but the mab-1 and mab-2 products are required for this stabilization, suggesting that the 1a, 2a, mab-1, and mab-2 proteins may directly interact (13). 1a also leads to a dramatic stabilization of RNA3, suggesting that it may bind directly to RNA3 (14). Because assembly of active replicase complexes requires the presence of one of the promoters in RNA3 (15), one model consistent with these data is that the active replicase com-

plex consisting of host factors (including mab-1 and -2) as well as proteins 1a and 2a assembles on the promoter.

Because the yeast genome has been entirely sequenced and the technology for dealing with yeast genetics is well advanced, it will be relatively straightforward to identify the mab-1, -2, and -3 proteins, and progress in this direction is being made (16). Ultimately, it should be possible to identify all of the host proteins required for replication of BMV RNA in yeast and, by extension, proteins required for the replication of the RNAs of the Sindbis-like viruses in plant and animal cells. Elucidation of the functions of these proteins will require further study and will be complemented by efforts to purify viral replication complexes. In addition to increasing our understanding of the interplay between virus and host during replication, such studies should deepen our knowledge of cell replication as well, in the same way that studies of retro-

viral oncogenes led to a new understanding of eukaryotic cellular control functions.

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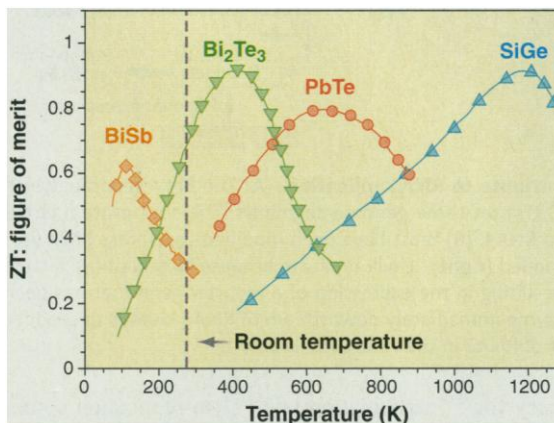
PERSPECTIVES: THERMOELECTRIC MATERIALS

Holey and Unholey Semiconductors

Terry M. Tritt

Cooling electronic devices can often be necessary to optimize performance. Traditional approaches to cooling are typically based on thermodynamic cycles involving compression and expansion of refrigerant gases (such as Freon). The heat required for vaporization is drawn from the materials or the volume (for example, a refrigerator) that is to be cooled. Thermoelectric (TE) materials, in contrast, do not rely on chemicals or gases but rather on a special physical phenomena called the Peltier effect, which is explained in detail below (1). In TE materials, heat is not primarily transported by the lattice but by the electrical charge carriers—electrons or holes. Applying an electrical current through a TE material cools one end and transports the heat to the other end of the material or device. This has distinct advantages in that it is solid-state refrigeration, without moving parts and vibrations, and with quiet performance and the ability for localized “spot” cooling. This can be very important for many semiconducting and other electronic devices. But until recently, the efficiency of TE devices has been frustratingly low, and applications remain limited.

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The dart board. The figure of merit, ZT as a function of temperature for current state-of-the-art thermoelectric materials.

Now, new TE materials aimed primarily at refrigeration applications have suddenly become “hot.” Several promising approaches were discussed in a symposium at the 1998 Fall Materials Research Society (MRS) meeting held in Boston (2). In his introductory talk, Glen Slack (Rensselaer Polytechnic Institute) characterized the materials as “holey” or “unholey,” depending on how good electrical conductivity and poor thermal conductivity were achieved in the same material—the key to a good TE material. This

concept is related to Slack’s earlier assertion of a “phonon-glass/electron-crystal” model (3, 4), which suggests that a good TE material should have the electronic properties of a crystalline material and the thermal properties of a glass.

To understand these concepts, first consider what makes a material a good TE. TE energy conversion is related to that found in the more familiar thermocouples, in which contacts between dissimilar metals or semiconductors result in a voltage difference (ΔV) that depends on the temperature gradient (ΔT) (this is called the Seebeck effect). When an electric current passes through a TE material, the Peltier heat transported by the charge carriers leads to a temperature gradient, with heat being absorbed on the cold side and rejected at the heat sink. The result is electronic refrigeration. Conversely, an imposed ΔT will result in a voltage or current and thus in small-scale power generation (5). The potential of a material for TE applications is determined by the material’s dimensionless figure of merit, $ZT = (\alpha^2 \sigma / \lambda) T$, where α is the Seebeck coefficient or thermopower ($\alpha \sim \Delta V / \Delta T$), σ is the electrical conductivity, and λ is the total thermal conductivity ($\lambda = \lambda_L + \lambda_E$, where λ_L and λ_E are the lattice and electronic contributions, respectively). The electronic component or power factor, $\alpha^2 \sigma$, is typically optimized as a function of carrier concentra-

tion through doping to give the largest ZT. High-mobility carriers are most desirable in order to reach the highest electrical conductivity for a given carrier concentration.

For many years, most research into thermoelectrics focused on the Bi_2Te_3 and $\text{Si}_{1-x}\text{Ge}_x$ systems (1, 5–7), the current state-of-the-art TE materials for use in refrigeration (down to T of about 250 K with Bi_2Te_3) and power generation ($T > 700$ K with $\text{Si}_{1-x}\text{Ge}_x$). However, there is substantial room for improvement (8). For example, low-temperature ($T \leq 220$ K) TE devices could revolutionize the computer ("cold computing" for enhanced performance), electronics, and infrared detector industries. Today's best TE materials, such as Bi_2Te_3 , have a ZT value of ~ 1 (see figure), a value that has remained the upper limit for more than 30 years. Several applications only become practical for $\text{ZT} > 2$, and at a ZT of 3, TE materials would become competitive with vapor-compression refrigeration systems such as home refrigerators and car air conditioners.

Slack's concept of holey semiconductors for new TE materials centers around minimizing the lattice thermal conductivity of a material by inserting loosely bound atoms or "rattlers" into voids or holes in the structure. These rattlers will move or bounce around inside these voids and thus scatter phonons (quantized lattice vibrations), effectively reducing and possibly minimizing the lattice thermal conductivity. Much of the recent work on materials called skutterudites (Brian Sales, Oak Ridge National Laboratory; David Johnson, University of Oregon; and Glen Slack), which recently broke the 30-year drought in new TE materials (9), and on "cage-like" materials called clathrates (George Nolas, Marlow Industries; Glen Slack; and Galen Stucky, University of California at Santa Barbara) use this concept. When the voids or cages in these materials are filled with "rattler atoms," the materials exhibit very low thermal conductivity ($\lambda < 1.5$ W/m-K) (10, 11).

Brian Sales introduced the concept of investigating TE materials by measuring atomic displacement parameters derived from x-ray diffraction data. These data can give details about the vibration amplitudes of the individual atoms and thus their potential for scattering different phonon modes, which determines thermal conductivity. New synthesis techniques of metastable phases, such as that of David Johnson, are currently being applied to acquiring entirely new phases of some skutterudite materials. John Badding (Pennsylvania State University) reported on "pressure tuning" TE materials. He subjects the materials to high pressure ($P \sim 2$ GPa) and has observed substantial improvements in

their power factors. Structural characterization can then provide insight into how to chemically dope the parent material to achieve similar effects at ambient pressures.

Results on "half-Heusler" alloys, which are intermetallics (for example, ZrNiSn), were presented by three groups [Ctirad Uher, University of Michigan; Bob Cava, Princeton University; and Valerie Browning (V.B.), Naval Research Laboratory (V.B. in collaboration with Joe Poon, University of Virginia, and Terry Tritt, Clemson University)]. These materials show very favorable electrical properties but currently exhibit thermal conductivity values that are too large. These materials do not have voids in their structures, relying on unholley approaches to reduce lattice thermal conductivity. For example, adding other elements to yield four- and five-element compounds can lead to mass-fluctuation scattering of the phonons. Quasi-crystals are also representative of the unholley group of materials; as a result of the complexity of their structures, they already exhibit glasslike thermal conductivity. Here, the challenge lies in improving their electronic properties (Terry Tritt, Roy Littleton, and Joe Kolis, Clemson University). Another approach uses composite materials consisting of nanophase metal (Ag) embedded in a conducting polymer matrix (George Johnson, Integrated Electronics). A reasonably large temperature gradient can be established in these materials by passing a current through the composites. The mechanism behind the observed behavior is not currently understood.

Other unholley materials that are currently being investigated for their TE properties include naturally occurring low-dimensional structures such as the chalcogenides (for example, CsBi_4Te_6 , presented by Mercuri Kanatzidis, Michigan State) and the pentatelluride materials (HfTe_5 and ZrTe_5 , Terry Tritt, Ray Littleton, and Joe Kolis). Interesting results on some ternary telluride (for example, Tl_2SnTe_3) systems were presented by Jeff Sharp (Marlow Industries). The chalcogenide materials can be viewed as "filled Bi_2Te_3 " materials. Selenium-doped pentatellurides far exceed the power factors of Bi_2Te_3 materials at low temperatures. Both of these groups of materials show very promising low-temperature electronic properties and may hopefully lead to low-temperature ($T < 220$ K) TE materials.

Other approaches use thin film or nanostructured materials on the basis of the concept of thermionic emission for TE cooling (Jerry Mahan, Oak Ridge National Laboratory; and Al Shakouri, University of California at Santa Barbara). A small gradient (~ 1 K) is established between each layer in a superlattice structure. The

gradient then increases with the number of superlattice layers. To achieve good TE properties, a relatively low work function material must be used, and charge carrier transport should be ballistic (that is, transport occurs without scattering) (12). Results based on superlattice structures were also presented by Rama Venkatasubramanian (Research Triangle Institute), who reported ZT values of > 2 using a $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattice. However, measuring the electrical and thermal conductivities accurately in thin films can be difficult, and therefore these results must be replicated and confirmed. Millie Dresselhaus' group at the Massachusetts Institute of Technology was among several who presented results on Bi nanowires and quantum well systems. Enhanced power factors, with $\text{ZT} > 3$, have been predicted for these materials through quantum confinement (13). High Seebeck values were reported in carbon nanotubes by Peter Eklund (University of Kentucky). Other low-dimensional structures were based on confinement concepts that use opal-like structures (Anvar Zakhi-dov, Allied Signal).

Many of the different approaches—thin films and bulk materials, holey and unholley semiconductors, and others—currently pursued in the search for improved TE properties are showing promise. The development of the next generation of TE materials, especially for TE cooling well below room temperature, could tremendously alter a number of high-tech industries. Although a clear frontrunner cannot yet be identified, the diversity of approaches suggests that we may not need to wait another 30 years for the next generation of TE materials.

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14. The MRS and financial supporters of Symposium Z, as listed in the proceedings (2), are gratefully acknowledged. Much of the research highlighted in this article was supported by Defense Applied Research Projects Agency, the Army Research Office, or the Office of Naval Research.