Electricity from **Hot Air**

Even the most efficient motor generates more heat than propulsion. Thermoelectric generators, however, could convert some of this unused energy into electricity – something that **Juri Grin** and his colleagues at the **Max Planck Institute for Chemical Physics of Solids** in Dresden are hoping to achieve. They are currently searching for particularly suitable materials for this endeavor.

TEXT **CHRISTIAN MEIER**

The terms Juri Grin uses sound strange. He talks about recycling or harvesting waste heat. Waste recycling, yes – that is commonplace. But waste heat recycling? And harvesting apples, okay, but how does one harvest waste heat?

Juri Grin thinks this is absolutely imperative. "We humans allow ourselves a great luxury," says the Director at the Max Planck Institute for Chemical Physics of Solids in Dresden. "We convert only around one third of the primary energy contained in coal, gas or oil into usable energy such as electricity or heat to heat our homes, for example." The rest escapes unused into the atmosphere as waste heat. "We can no longer afford to do this, if for no other reason than that of climate change," says Juri Grin.

To change this situation, the chemist and his colleagues are working on a particular way to recycle waste heat. The fundamental idea is that thermoelectric materials, or thermoelectrics for short, will convert at least some of the energy that currently goes unused into electricity. There are various chemical compounds that can be used for this. Juri Grin's team of researchers at the Max Planck Institute in Dresden is investigating two special classes of these substances.

A TEMPERATURE DIFFERENCE CREATES THE VOLTAGE

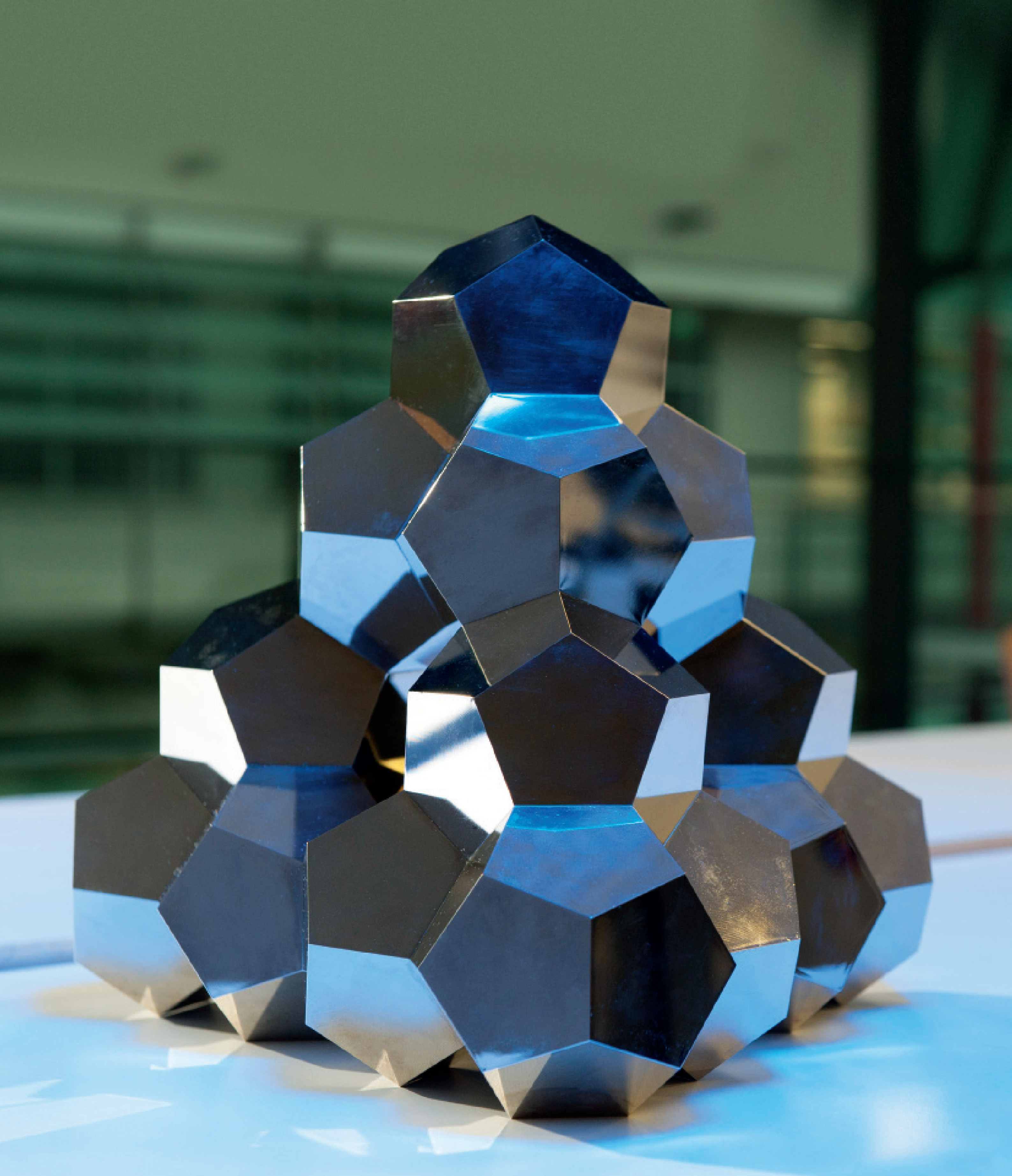
Materials that convert heat into electricity have been known since the beginning of the 19th century. Physicist Thomas Johann Seebeck discovered them quite by accident. Thermoelectrics, which consist of electrical conductors or semiconductors, have also been in use in technical applications for some time: each thermocouple makes use of the thermoelectric effect to measure temperature. These materials also produce electricity, especially where other power sources are not available, or where the power source used must suffer no wear and tear, thus not requiring maintenance – in space probes that orbit distant planets and moons, for instance.

Inside the probes, a radioactive substance decays in a reactor, generating a temperature of several hundred degrees Celsius. The temperature in space is below minus 270 degrees. The resulting temperature difference of more than 1,000 degrees provides ideal conditions for generating electricity with a thermoelectric material incorporated into the hull of the probe, surrounding the radioactive core, because it is precisely this kind of temperature gradient that promotes thermoelectric energy conversion.

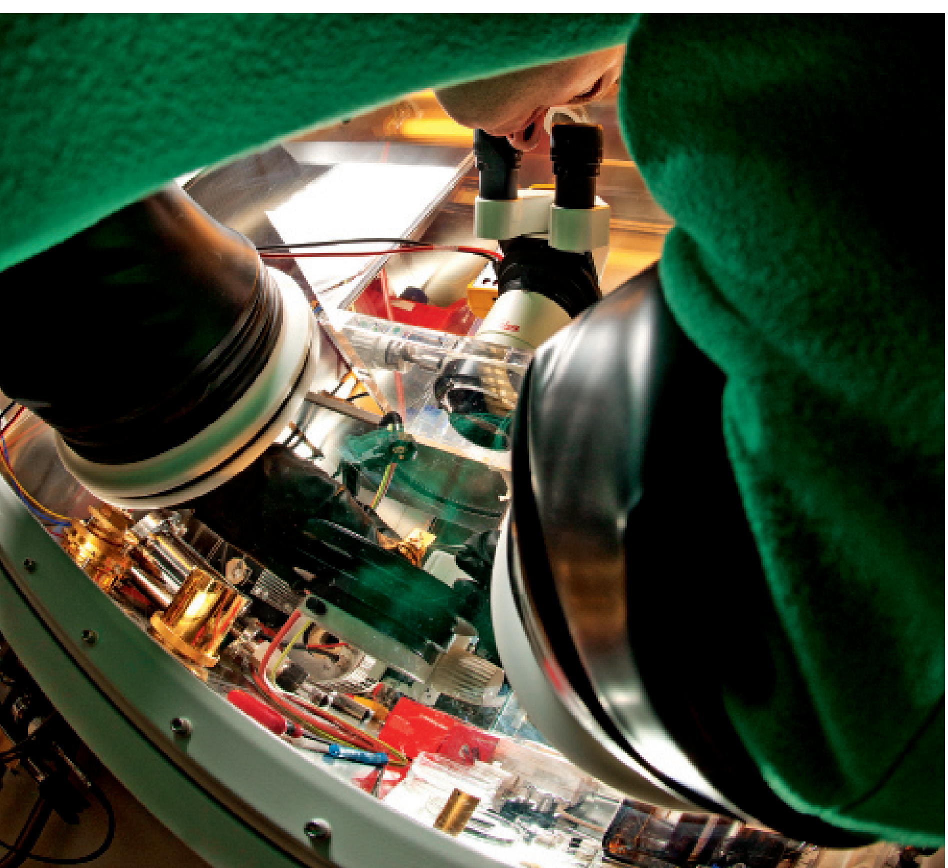
The temperature difference means that the charge carriers have a higher energy in hot parts of the material than in cold ones. This produces a voltage that increases as the difference in temperature increases.

The plan is for this principle of power generation to no longer be limited to such extreme applications as space travel, because cars and power stations also produce ample heat that currently escapes unused. For this reason, in 2008, a German automotive manufacturer installed a thermoelectric generator in a test vehicle. It converts part of the heat of the exhaust gas into electricity for the onboard electronics, thus saving fuel – a not inconsiderable 5 to 8 percent, according to the company. >

Photo: Bastian Ehl



Candidate for an efficient thermoelectric material: The crystal structure of intermetallic clathrates can be recognized in the model. One atom sits at each corner of the polyhedrons, and the cavities in their interiors provide room for further atoms. A voltage can be generated in such materials if they are exposed to a temperature gradient.



The great potential of such thermoelectric generators becomes evident with a simple calculation: if only 10 percent of the cars in Germany, or around five million cars, were equipped with a thermoelectric generator that produced one kilowatt of electric power, and if each of these generators were active 200 hours per year, 100 million liters of fuel could be saved.

The only problem with this promising scenario is that there are as yet no thermoelectric generators with sufficient power, as thermoelectrics currently don't convert heat into electricity very efficiently. Researchers all over the world, including Juri Grin and his colleagues, want to change this. They are developing thermoelectric materials that have as high a quality factor as possible.

THERMAL AND ELECTRICAL CONDUCTIVITY ARE COUPLED

The quality factor, or ZT for short, is a numerical measure of how effectively a material converts thermal energy into electrical energy, and depends on three physical quantities – it increases as the Seebeck coefficient increases. Named after the discoverer of thermoelectricity, this material characteristic indicates the voltage that is produced between the ends of a thermoelectric material for one degree difference in temperature. The quality factor also increases when the electrical conductivity is as high as possible. The electrical conductivity determines how

top: This instrument can be used to measure the electrical resistance of a sample. The material is examined in a noble gas atmosphere to protect it from oxygen.

bottom: Technician Ralf Koban prepares a sample holder in order to determine the thermoelectric properties. This involves working in a glove box filled with noble gas.

Photos: Bastian Ehl (2)

well the charge carriers flow through the material. Finally, the thermal conductivity determines how fast the temperature difference, which generates the voltage, is equalized. Thus, to achieve a high quality factor, the thermal conductivity of a material should be as low as possible.

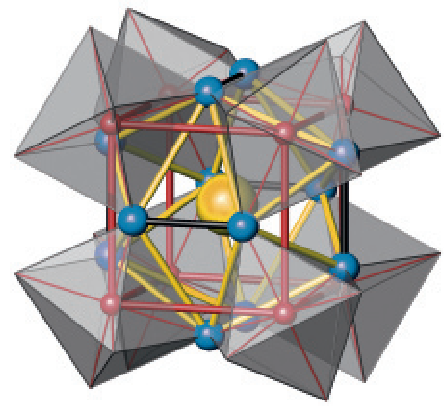
The aim is therefore to find or develop materials that have a high electrical conductivity but a low thermal conductivity. And that is precisely the problem: in conventional metals and semiconductors, thermal and electrical conductivity are coupled. Both properties are determined by the number of charge carriers, which transport current and also make a significant contribution to heat conduction.

The electrical conductivity can be changed, for instance, by introducing foreign atoms into the crystal lattice of a thermoelectric material. These foreign atoms contribute higher or lower numbers of electrons to the conducting electrons than the main components do. But what the quality factor gains from the increasing electrical conductivity is canceled out by the increase in thermal conductivity. Until the 1990s, the general opinion was that this seemingly unsolvable dilemma prevented efficient thermoelectric materials from being developed; the topic no longer generated any interest.

"But then materials were discovered whose electrical and thermal conductivity are partially decoupled," says Juri Grin. This offered a way out of the conductivity dilemma. And since it coincided with the optimization of further material characteristics, efficient thermoelectric generators suddenly seemed possible. The scientist thinks this stimulated research. The German Research Foundation is now also supporting this research in the "Nanostructured Thermoelectrics" priority program.

DIFFERENT CHEMICAL BONDING SOLVES THE DILEMMA

Juri Grin and his colleagues begin the search for efficient thermoelectric materials with a fundamental question: "We want to find out how the type of chemical bonding in a material affects its physical properties," explains Grin. So the researchers are investigating how electrical and thermal conductivity depend on whether the bonds are of an ionic nature – that is, based on electrostatic forces between ions – or whether neighboring atoms are bound together by shared electron pairs and form covalent bonds. They discovered that the two properties can be decoupled to a certain extent in clever combinations of ionic and covalent bonding. Understanding these relationships helps the scientists systematically synthesize thermoelectric materials with as high a quality factor as possible. >



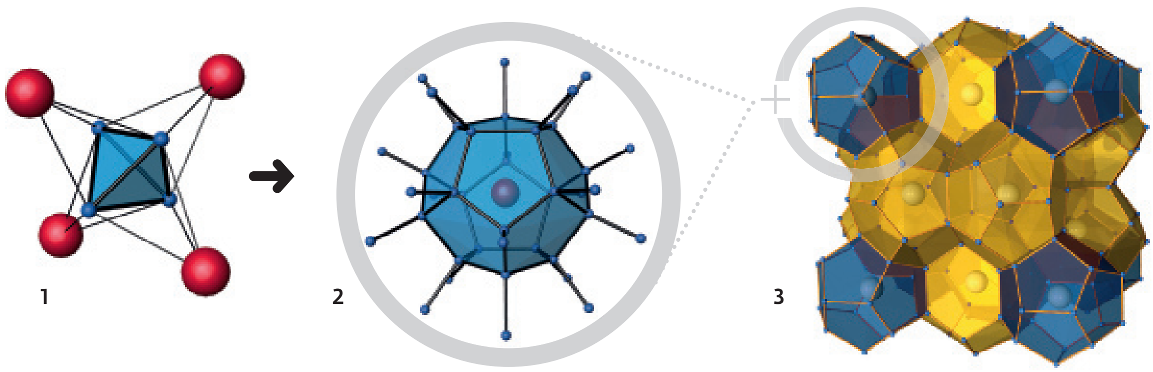
View into a skutterudite with filling: The red spheres represent cobalt, rhodium or iridium atoms, and the blue ones phosphorous, arsenic or antimony. Calcium or barium atoms (yellow) are located in the voids of the lattice. Octahedral structural elements are outlined in gray.

HOW A THERMOELECTRIC GENERATOR WORKS

The fundamental building block of a thermoelectric generator – a thermoelectric module – resembles the Greek letter "pi," consisting of two legs that are electrically connected. One of the legs is a so-called n-conductor (the n stands for negative), the other a p-conductor (the p stands for positive). While (negatively charged) electrons provide the current flow in n-conductors, this is done in p-conductors by positively charged charge carriers, so-called holes.

The module is hot at the top, so on the side of the bar, and cold at the bottom, at the ends of the legs. Since the electrons and holes at the hot end of each leg have a higher kinetic energy than those at the cold end, more charge carriers travel from the hot end to the cold end than move in the opposite direction in a given time. Negative charge thus collects at the cold end of the n-leg, and positive charge at the cold end of the p-leg. A thermoelectric device built in this way generates a voltage that can be used for technical applications. However, such a module produces too little current for most such applications, so many of them are connected in series, like batteries in a flashlight.

Graphic: MPI for Chemical Physics of Solids, Scientific Report 2009



Building chemical cages: The molecular building blocks (1) of the clathrates consist of silicon (blue) and a metal (red) such as sodium, potassium or barium. They form silicon polyhedrons (2), which surround the metal atoms like cages. The polyhedrons stack up to form a voluminous structure (3).

The researchers in Dresden consider two classes of materials to be particularly promising: filled skutterudites and intermetallic clathrates. The two classes of substances are composed of different chemical elements and have different crystal structures. Skutterudites consist of phosphorous, arsenic or antimony, as well as selected elements of the iron and cobalt group or the group of platinum metals. Clathrates, in contrast, contain elements of the fourteenth group of the periodic system, namely germanium and silicon, and of the thirteenth group, such as aluminum, or of the transition metals, such as nickel. Both the skutterudites and the clathrates are particularly interesting as thermoelectrics if they contain additional metal atoms or ions. These are located in cavities that are present in the crystal structures of the materials.

"We are aiming for a comprehensive understanding of these compounds," explains Juri Grin, because a high quality factor is not sufficient to recommend a material for generators in cars, for example. "It is also important that the material be at its most efficient between 300 and 600 degrees Celsius," adds his colleague Michael Baitinger, because the temperature of car exhaust gases is in this range. "The material must also remain stable over a long period of time at these temperatures," says the researcher. And it should not expand too much when it becomes hot, or it can hardly be permanently incorporated in a generator.

A material that fulfills these requirements can be identified only with an in-depth knowledge of chemistry and physics. "In addition to the effect of the chemical bonding, we must also understand how the physical properties depend on the type of structure," says Grin. The microstructure describes the form, size and chemical composition of the microscopically small grains that make up a solid.

ATOMS OSCILLATING IN THEIR CAGES

To begin with, however, the most important question is: how can electrical and thermal conductivity be influenced as separately as possible? Nature provides at least a starting point for the answer. After all, in a material, heat is transported not only by the free electrons, which also flow in an electric current. This component of the thermal conductivity necessarily increases with electrical conductivity. But heat is also conducted by sound waves, or, in the language of the scientists, by phonons, which travel through the material.

Absorbing phonons makes it possible to decrease the thermal conductivity without affecting the electrical conductivity. "We found that this is possible in materials that contain both covalent and ionic bonds," explains Grin, as is the case with intermetallic clathrates.

In the clathrates, for example, covalent bonds link most atoms of one or more types of elements to form a lattice: cavities that resemble soccer balls in shape and that are formed by pentagons or hexagons then stack up to form a delicate structure. The voids in the lattice accommodate ions of a different element. The charged particles sit there as if in a cage, trapped by the electric field of the clathrate lattice, meaning they form an ionic bonding.

The lattice of the covalently bonded atoms and the ions in the cages each play different roles. While the walls conduct the electric current, the ion in the cage scatters phonons that pass though the crystal lattice. If a phonon impacts on the cage, the ion is deflected from its most stable position in the center of the cage. This impulse causes it to oscillate in its cage like a bead in a child's rattle. This can be visualized by imagining that the oscillating ion absorbs the energy of the phonon just like a heavy metal sphere under a skyscraper absorbs the oscillations of the building during an earthquake.

Graphics: MPI for Chemical Physics of Solids (3)

left: Chemistry uses a voltage: Ph.D. student Xianjuan Feng prepares a reaction in an arc furnace. A voltage between two electrodes produces an arc with a temperature of several thousand degrees in which the starting materials react with each other.

right: Chemistry uses a current: In the induction furnace, a conducting coil generates eddy currents in the carbon crucible and the metallic starting materials, and heats them up in such a way that the chemical conversion takes place.

In more accurate physical terms, the heat excites the lattice of the covalently bonded atoms and the trapped ions to execute oscillations at different frequencies. The two oscillations damp each other so that the heat is not conducted well on this path. This mechanism can be enhanced without affecting the electrical conductivity.

This is precisely what Juri Grin and his colleagues achieved. They synthesized both clathrates and skutterudites with different compositions and tested their suitability as thermoelectrics. But rather than choosing randomly from the seemingly endless number of possible chemical compositions, the researchers first use quantum-chemical models of the chemical bonds in a compound. "In our calculations, we vary the chemical composition, the arrangement of the atoms and the crystal structure," explains Juri Grin.

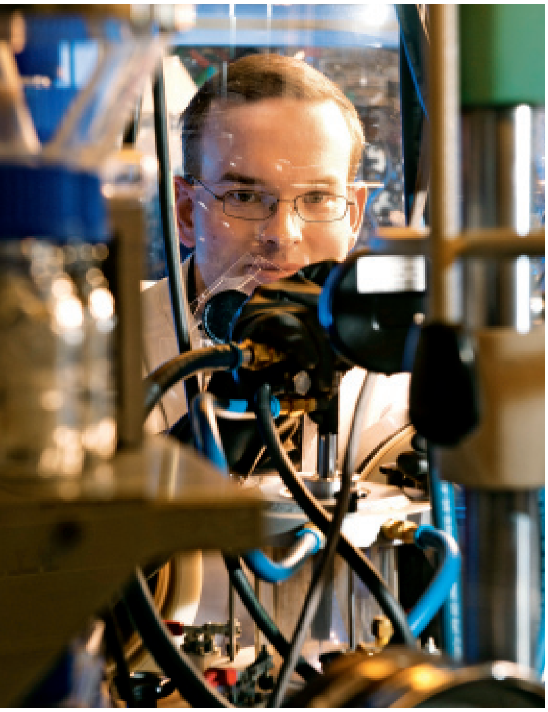
A STARTING POINT FOR EFFICIENT THERMOELECTRIC MATERIALS

The calculations show where in the crystal structure which type of bond – covalent or ionic – predominates. Compounds that are shown to crystallize in a covalently bonded lattice and whose voids surround ions are deemed to be promising candidates. The chemists are now trying to synthesize these and then analyze their precise composition and crystal structure. Together with their colleagues from Frank Steglich's Solid State Physics department, they are also determining the physical properties on which the quality factor depends.

Over the years, the researchers have thus identified and produced clathrates whose quality factors are comparable with the bismuth telluride that is already used in practice. "We also see a possibility to develop even more efficient thermoelectrics with this approach in the future," says Juri Grin.

Meanwhile, the researchers in Dresden are tackling another problem that could prevent the technical application of the clathrates and skutterudites: their manufacture. For laboratory purposes, the chemists usually synthesize these substances by direct reaction of the starting materials through melting

Photos: Bastian Ehl (2)



Bodo Böhme often produces new compounds in the arc furnace (left), but he and his colleagues also test other synthesis methods (right): Here, Böhme presents a sample container containing the powders of starting materials. A gas flows over them and they react to form the target compound.

or solid-state reactions. But it takes a lot of effort before this method provides the desired material, and then it yields only relatively small quantities. The product usually does not have a uniform composition because all sorts of atomic arrangements are created in the melt. A material must thus undergo subsequent treatment with heat for days, weeks, or sometimes even months, making this method completely useless to industry.

"We wanted to further develop the preparation methods by having the starting materials react with each other in solid form," explains Bodo Böhme, whose work focuses on the synthesis. These methods allow chemists to produce new compositions of thermoelectric materials. They need only to get the starting materials to strike up a chemical relationship when the substances are lying grain to grain and not getting involved with each other.

In different approaches, the Dresden-based researchers initially gathered indications that even solid materials can be moved to react – when they tested the spark-plasma sintering method, abbreviated SPS, for example. This method is already used in industry for the densification of metallic or ceramic powders and the formation of parts with a defined shape. A strongly compacted powder is processed with DC pulses that are only a few milliseconds long but very powerful, so that the powder grains slightly deform and fuse together.

A CHEMICAL AGENT IMPROVES CONTROL

"We discovered that it is also possible to do chemistry with this technique," says Grin. Under the conditions created with the SPS method, the atoms can wander to and fro between the grains and undergo reactions. But this method is not suitable for the large-scale industrial production of thermoelectrics because, like the melting, it provides only individual samples whose properties may also differ slightly from one another. Industry would like to have a method that operates continuously, churning out the finished material like gravel on a conveyer belt.

Even during their experiments with plasma sintering, the chemists also tested means other than pressure and current pulses to force the solid starting materials to react. Eventually, the method of choice – at least for the production of the clathrates – proved to be to use an oxidizing agent – hydrogen chloride gas, to be precise. The researchers feed the gas, which produces hydrochloric acid when dissolved in water, into a reactor containing a powder of the starting substance. As the oxidizing agent now wafts over the starting compound containing all elements involved, it triggers the chemical partner selection.

"This technique opens up a new chapter in the preparation of metallic materials, such as the clathrates," says Juri Grin. It allows chemists to influence the composition of thermoelectric materials more accurately than before.

Exactly which atoms are incorporated is decisive for the number of electrons that contribute to the con-

Photos: Bastian Ehl (2)

ductivity. The method can also be realized on an industrial scale.

Their comprehensive approach thus enabled Juri Grin's team of researchers to increase the efficiency of the thermoelectric materials, while at the same time making them easier to handle during their industrial production and actual application. To this end, they are collaborating with the Fraunhofer Institutes for Manufacturing Technology and Advanced Materials (IFAM) and for Ceramic Technologies and Systems (IKTS).

In this cooperation, which is supported by the Free State of Saxony, the Max Planck researchers are searching for the suitable thermoelectric materials and methods to produce them. The IFAM researchers form the powdery substances obtained in this process into work pieces that can be incorporated in generators. Staff at the IKTS design the generators for this. Juri Grin and his colleagues are thus slowly approaching their goal of recycling waste heat with thermoelectric generators – and maybe in a few years, this expression will no longer sound so strange. ◂

GLOSSARY

Thermoelectric quality factor
A measure of how well a material converts thermal energy into electrical energy.

Seebeck coefficient
Indicates the voltage created between the two ends of, for example, a rod of thermoelectric material if their temperature differs by one degree.

Group of the periodic system
Comprises the chemical elements in a given column in the periodic system of the elements (PSE), such as the halogens or the noble gases. The elements in a group have similar properties, but become more metallic the further toward the bottom of the PSE an element is.

Intermetallic clathrates
Usually consist of elements of the third and fourth main group of the PSE. They form (often together with transition metals) a voluminous framework for the crystal structure whose voids provide space for atoms or ions of further elements, such as alkali, alkaline earth or rare earth metals.

(Filled) skutterudites
Consist of elements of the fifth group of the PSE and a transition metal of the iron, cobalt or nickel group. Their crystal structure has cavities that provide space for further atoms or ions.