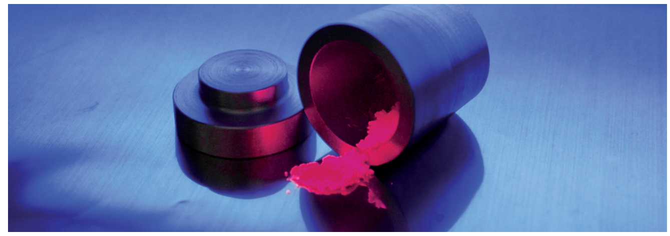
Chemistry

Bright lights, big business

By Hanno Charisius



The newly developed phosphor enhances the quality of color rendition by white-emitting LEDs.
Source: Professor Wolfgang Schnick, LMU Munich

Unlike sunlight, white light from most artificial sources is perceived as cold. Wolfgang Schnick's team at LMU is creating chemicals that enable LEDs to deliver high-quality white light.

Several times a week, Wolfgang Schnick's co-workers at LMU's Laboratory of Inorganic Solid-State Chemistry in Grosshadern set out to find gold – sorting through small piles of multicolored grit that looks vaguely like shell sand, using tweezers, tiny metal spatulas and, if necessary, a microscope. But the nuggets they seek don't have a golden sheen; they glow in a range of different colors.

These chemists are engaged in a quest for new materials, for chemical compounds that no one has ever seen before. To find such exotic substances, the researchers need to create them first, because they have never existed naturally on our planet. So they take a few basic ingredients like silicon and nitrogen, and add some of the rarer chemical elements to the mixture. They then transfer small portions of the mixture to thick-walled, lidded crucibles made of tungsten, each about the size of a shot glass, which are placed in a furnace held at over 1,000 degrees Celsius for a day. What comes next has lost none of its excitement for Schnick after 20 years: The lids are taken off and the chemists get their first look at what has happened in the reaction vessels. Every time, they hope to discover something comparable to what Schnick and his former colleague Hubert Huppertz, now Professor of Chemistry at Innsbruck University, found in 1997.

Back then, when the pair opened their crucible, it shone with a reddish glow. "We were absolutely thrilled," says Schnick, recalling that magic moment. All they had done was to add one further ingredient to an already known recipe – the element europium. In the absence of this rare-earth metal, the mixture reacted to give a compound that was pale gray in color, but the addition of europium caused the product to glow when exposed to daylight. "And we knew that this compound would be very stable, unlike the short-lived dyes used in marker pens, which fade if they are left for a few days on the window sill," Schnick adds.

Helping LEDs to break into the huge global market for domestig lightning

To begin with, he and Huppertz believed they had come across a new pigment, which might interest car manufacturers. But they soon worked out that a gram of their red substance would cost more than the same amount of gold!

At that point, the new compound seemed destined to be filed away, like countless other chemically interesting synthetic substances, among those that never find any practical use. However, shortly after he and Huppertz had published their findings, Schnick received phone calls from two researchers who worked for prominent manufacturers of lighting devices. They expressed great interest in the red pigment, because they felt it might solve a long-standing problem: How to create a diode that emitted warm white light like sunlight or the light from a conventional lightbulb, instead of the cold radiance that is familiar from car headlights, streetlamps or torches. For this was the drawback which at that time prevented LEDs from breaking into the huge global market for domestic lighting.

LEDs (short for 'light-emitting diodes') are made up of minute semiconductor crystals, which emit light when connected to a source of electric current. Depending on the composition of the semiconductor, they produce light only in narrow color bands, in red, orange, yellow, green, blue or violet. Only by mixing different colors could white light be generated. Unfortunately, this light looks quite unnatural and shows poor color rendition.

However, the europium-containing compound from Schnick's laboratory, white light of a much higher quality, not very different from that produced by a standard light-bulb, could be created.

For the substance converts energy-rich, short-wave ultraviolet or blue radiation into light of longer wavelengths – toward the red end of the visible spectrum – by a phenomenon known as luminescence. And irradiating a panel containing both Schnick's compound and a second, green luminescent material, results in the emission of light that the eye perceives as a warm white.

Moreover, this kind of light source consumes only a small fraction of the energy required by a traditional light-bulb. "The incandescent bulb was one of Thomas Alva Edison's terrific inventions," says Schnick, "but it produces far more heat than light – around 20 times as much, in fact." That's why scientists and engineers have spent decades trying to develop light sources that emit more light and less heat, and this work gave us the fluorescent tube and the compact fluorescence lamp. In both cases, a gas discharge produces light. But since these devices contain toxic and environmentally harmful amounts of mercury and emit light of relatively poor quality, they have always been seen as a stop-gap solution.

In contrast, the principle behind the LED amounts to a technological revolution, and this year's Nobel Prize in Physics was awarded to three Japanese researchers for their contributions to the invention of the blue LED. Its significance is demonstrated by the fact that replacement of all the electric light sources currently in use with LEDs would reduce global consumption of electricity by 16%. "In Germany alone, all nuclear power stations could be immediately taken off the grid," says Schnick. His work thus makes a substantial contribution to the *Energiewende*. But that was not at all what he set out to do.

Schnick sees himself as someone who carries out basic research in the field of 'explorative solid-state chemistry'. He ventures into areas of the subject that no one has previously visited or even approached before. Intrepid adventurers may explore unknown worlds or prospect for valuable raw materials in the bowels of the Earth. The aim of Schnick's quest is to find ways of making materials never seen before. Schnick and his colleagues pursue this goal in a systematic way, but they cannot precisely control the outcome of their chemical syntheses. In other words, they are in search of something with only a vague idea of what it is. Like children playing with Lego blocks, they create conditions in which atoms can be linked together to form complex compounds, hoping to find something useful or at least interesting among the reaction products. "We approach our syntheses without preconceptions, with no particular application in mind," Schnick says. And sometimes, he adds, one is lucky and something turns up that can change the world.

The principle behind the LED amounts to a technological revolution

It all began with an experiment that Schnick regarded with a skeptical eye. Hubert Huppertz wanted to take some well-known compounds consisting of nitrogen, silicon and either barium or strontium and add some europium to them, simply because the element was about the right size to take the place of strontium or barium atoms in the crystal lattice. "At the time, I couldn't understand why he wanted to do that," Schnick admits. "I never expected it would lead to such an exciting find." But he had just been awarded a Leibniz Prize by the German Research Foundation (DFG) and was free to use the prize money for his research. "That meant that we could actually afford the europium, which is extremely expensive."

They hadn't thought out what effect the replacement of a small fraction of the atoms in the starting compound might have, they just did the experiment. "The element of play, of trying things out, is important," says Schnick. Sometimes, even mistakes, such as errors in weighing out reactants, can lead to intriguing surprises.

What actually goes on in their crucibles during the hours in which a reaction may proceed is difficult to tease out. The localized fusion of metals on a microscopic scale probably plays an important role in the formation of novel materials. Interactions with reactants in the vapors that form under these conditions may also be involved. At all events, itinerant atoms need time to find their places in an ordered crystal lattice, and chemists need to be patient. Having to wait for a day or two is not at all unusual. In other areas of solid-state chemistry, reactions can sometimes run for months.

Only when the waiting is over the result can be inspected – if there is one. Most of the time, what one sees is not nearly so spectacular as the first sight of that europium-containing compound. One might find an uninteresting major product and a smattering of differently colored byproducts – like raisins in a cake. Often the outcome looks like beach sand. Then the researchers have to examine the heap under the microscope and laboriously pick out the more interesting grains.

These then have to be investigated more thoroughly – first by spectroscopy, which reveals the compound's optical properties, and then by X-ray crystallography. "A method that was

Research

discovered at this university over a century ago," Schnick points out. Indeed, Max von Laue won the 1914 Nobel Prize in Physics for his discovery of the diffraction of X-rays by crystals. Chemists have since used it to determine the spatial arrangement of the atoms in newly synthesized compounds. Equipped with this knowledge, Schnick's team can begin to modify their reaction (by)product and try to endow it with properties required for a specific application.

At this stage they often have to design innovative synthetic routes. "That's why it's a good thing to have new students regularly joining the group. They bring in new ideas and unconventional thinking, and both are necessary for scientific discoveries. It was this kind of uninhibited approach that led Hubert Huppertz to the idea of adding europium to his reaction mixture.

Reducing energy consumption

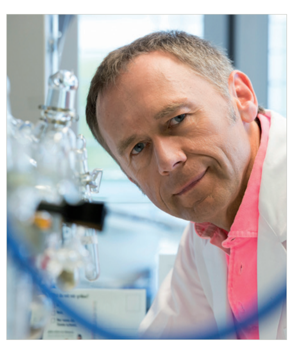
By the time the first products containing the new luminescent compound were manufactured, more than 10 years had passed since its discovery in 1997. It took that long to modify the synthetic process so that the compound could be made in amounts large enough for industrial use. Instead of microgram amounts, the modified process could produce up to 500 grams of the luminescent substance in a single run.

Only a few years ago, the first LED lamps capable of emitting warm white light cost up to 35 euros apiece and weren't very bright. Now the cost of a lamp that can easily replace an old-fashioned 60W bulb, and consumes far less energy, has fallen to less than 10 euros. A classical incandescent bulb produces a maximum flux level of 15 lumens per watt of electric power. Today's LEDs reach levels above 200 lumens per watt. But Schnick still sees lots of developmental potential in the LED. Take the color rendition index (CRI), which is a measure of how similar the emitted light is to natural sunlight. A value of 100 corresponds to the quality of sunlight, and only very good incandescent lamps reach that value, says Schnick. LEDs made with the europium-containing material now reach a value of 83, scores for most low-energy light bulbs lie well below 80. Meanwhile, Schnick's team has come up with a new material, made up of lithium, aluminum, strontium, nitrogen and a smidgen of europium. It allows for better tuning of the emission spectrum, raising the CRI to 93 and reducing energy consumption by another 14%.

The researchers only came upon this new substance in one of their crucibles in December 2012, but preparations are already underway for its market launch. "The timespan between the discovery of a new material and the manufacture of a marketable product has been drastically reduced," says Schnick. This is in part the result of increased international competition. "Business is booming, and the number of groups working in this area has risen substantially." Nevertheless, the truly innovative laboratories, those that have discovered the most important luminescent materials in recent decades, remain few and far between.

Schnick is particularly pleased when he finds the results of his work in consumer products. The flash in his smartphone, which enables flesh tones to be reproduced more realistically than before, is one such example. His inventions can also be found in indicator lights, as well as in more and more homes. He himself decided to delay replacing the conventional light bulbs in his own home, because he was of course aware that much better LEDs would soon be on the market.

Schnick has ideas for many other applications for the new light sources but, since he doesn't want to give competitors any hints, he prefers to keep them under wraps for the moment. And even when every last bulb in the world has been replaced by an LED, he will still have plenty to do. We will continue to engage in basic research, synthesize new compounds and explore their practical potential, he says. "The hunt for novel materials will never lose its fascination for me."



Prof. Dr. Wolfgang Schnick
Holds the Chair of Inorganic Solid-State Chemistry at LMU. Born in 1957, Schnick studied Chemistry and obtained his doctoral degree at the University of Hannover, later worked at the Max Planck Institute for Solid-State Research and completed his *Habilitation* at Bonn University. He served as Professor of Inorganic Chemistry at Bayreuth University, before moving to Munich in 1998. In 1996 he was awarded a Leibniz Prize by the *Deutsche Forschungsgemeinschaft*, and was a nominee for the German Future Prize in 2013.

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