c&en
CHEMICAL & ENGINEERING NEWS
NOVEMBER 19, 2018

How should benefits from DNA data be shared?
P.16

Natural versus synthetic routes to cannabinoids
P.20

The search for better white light

Advances in inorganic phosphors boost the efficiency and appeal of LEDs
P.28

ACS
Chemistry for Life®

Tuning phosphors for better white light

Advances in the inorganic powders boost the efficiency and appeal of LED bulbs

MITCH JACOBY, C&EN CHICAGO

In brief

Light-emitting diodes (LEDs) that produce white light are about to take over the lighting world. The U.S. market share of these super-long-lasting, cool-to-the-touch lights, which use less than a quarter of the energy of conventional incandescent bulbs, sits around 10%. Industry watchers predict that number will exceed 80% by 2030, reducing power consumption in the U.S. by 40%. Chemists are taking a leading role in this technology, which underpins general lighting and electronic displays, by customizing the emission spectrum, stability, and other properties of inorganic phosphors in the LEDs that help produce finely tuned white light.

"Incandescent bulbs are one of the most energy-inefficient products in daily use," Joanna McKittrick says. Touch a regular old 100-W light bulb after it's been lit for a few minutes, and you'll see what she means.

Less than 5% of the electrical energy that goes into the tungsten filament inside is converted to visible light, explains McKittrick, a luminescent materials specialist at the University of California, San Diego. The rest is wasted as heat that, should you follow our instructions, will burn your fingers.

Incandescents "basically haven't changed since Thomas Edison invented them" about 140 years ago, she says.

Colorful inorganic phosphors, such as the ones synthesized at Ludwig Maximilian University Munich shown here, work in concert with LEDs to produce white light.

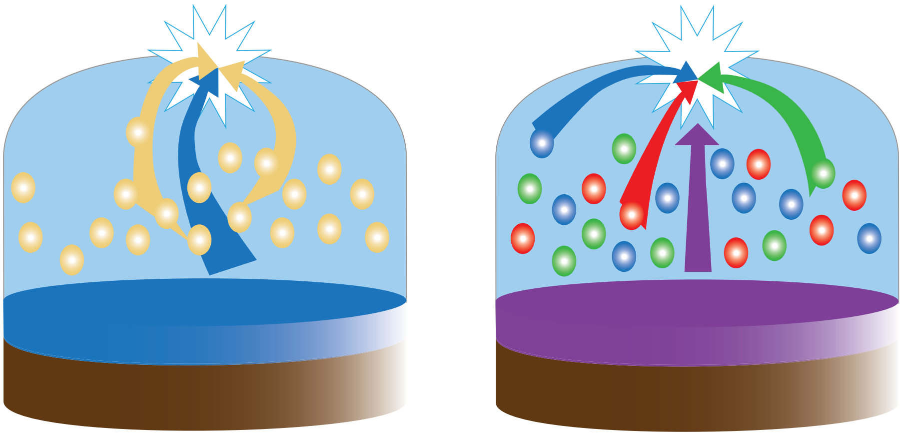
CREDIT: CHRISTIAN MAAK AND PHILIPP STROBEL/LMU MUNICH

Bulbs that contain light-emitting diodes (LEDs), on the other hand, can produce the same amount of white light but barely feel warm to the touch. That's because LEDs are more energy efficient. A 15-to-20-W LED can produce the same brightness as a 100-W incandescent, roughly 1,500 lumens. LEDs are also less fragile and can last tens of thousands of hours longer. Nevertheless, these modern alternatives currently account for less than 10% of lighting worldwide, according to data from the U.S. Department of Energy.

That number is projected to grow explosively in the next few years. LED purchase prices are falling quickly. Five years ago, a 100-W-equivalent LED bulb could cost 10 times as much as an incandescent, which sold for about $1. A cursory search of Amazon shows that the price of some LED bulbs today is about $3. As LED prices continue to fall, researchers are working to further reduce the power they consume and improve the color quality of light that the bulbs emit.

Despite the benefits of LEDs, incandescents still win out when it comes to their light quality. The old-school bulbs produce a white hue that more closely mimics sunlight than the bluish tinge of LEDs.

To make LEDs that are more pleasing to consumers for home use, scientists are developing new phosphors. These are inorganic compounds, often applied to the resin-based dome-shaped cap covering an LED, that can alter the light emitted, giving it a more pleasing hue. Combined with improvements to energy efficiency and stability, the advanced materials will benefit not only general lighting but also electronic display technology and other applications.



Phosphor-converted LEDs generate white light by blending light of various colors. In one commercial design (left), light from a blue-emitting LED excites a yellow phosphor. Blue and yellow combine to make white light. In another design (right), UV light (depicted as purple) excites red, green, and blue phosphors to make white.

DOE forecasts that by 2030, for general lighting, LED use will exceed 80%. That growth could reduce power consumption by 40%, saving more than $25 billion at today's energy prices and reducing power-plant emissions of CO_2 by more than 160 million metric tons.

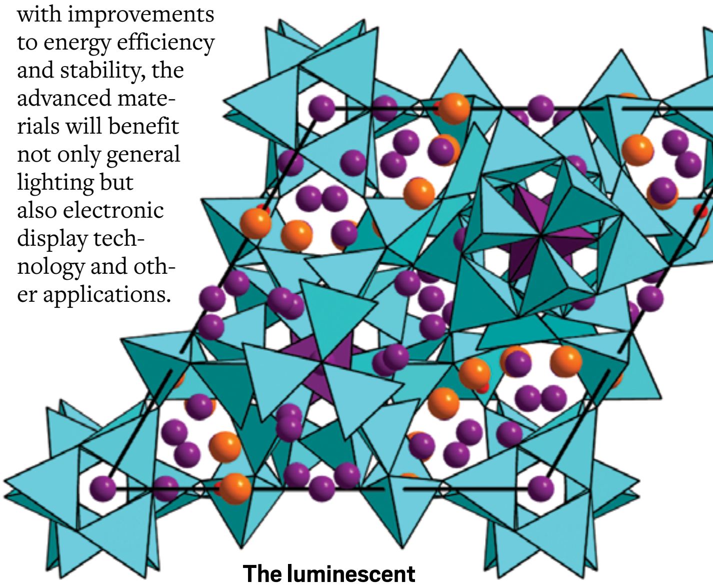
Making white light

Compared with LEDs, incandescents have "very good color rendition," says Peter J. Schmidt, an LED and phosphor specialist who works at the Aachen, Germany, research center of Lumileds, a lighting company. That means the perceived colors of objects viewed under incandescent lighting appear "correct," or very close to their appearance in daylight. To put it in lighting parlance, incandescents have a color rendering index (CRI) of 100, the same as sunlight.

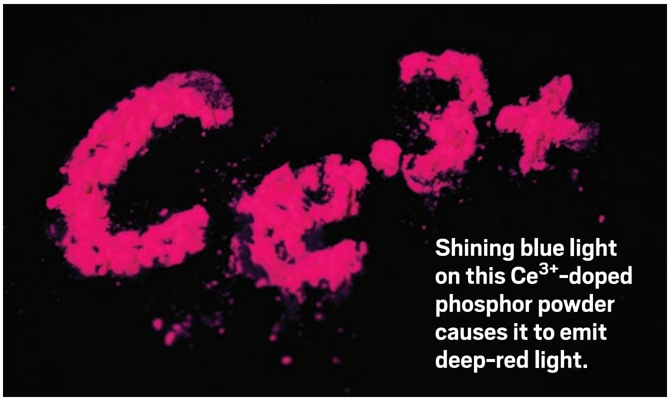
In contrast, some white LEDs cast bluish light, which many people find unsatisfying for residential lighting. These lights also have a lower CRI, which causes the colors of things they illuminate to appear unnatural to the eye. Bluish LED light can also cause subjects in photos and videos to look peculiar.

The specific tone of the white light emitted by an LED depends on how the device makes the light. The range of possibilities is usually described by a color label and a temperature, a value that historically comes from black-body radiation physics, in which an object's temperature correlates with the spectrum it emits. The various types of white LED lights are classified as a reddish-orange "warm white" (about 3,000 K), a neutral or faintly blue "cool white" (about 4,000 K), and a blue-white "daylight" (about 6,000 K).

One approach to making white light calls for blending the blue, green, and red outputs of three single-color LEDs, each based on a different semiconductor. In practice, that strategy can be cumbersome and expensive, requiring complex circuitry to control the color output.



The luminescent phosphor depicted above and to the right emits deep-red light. Black outline = unit cell. Turquoise = SiN_4 tetrahedra. Violet = LiN_4 tetrahedra. Red = O and F. Purple = Li. Orange = La, Ce, or Y.



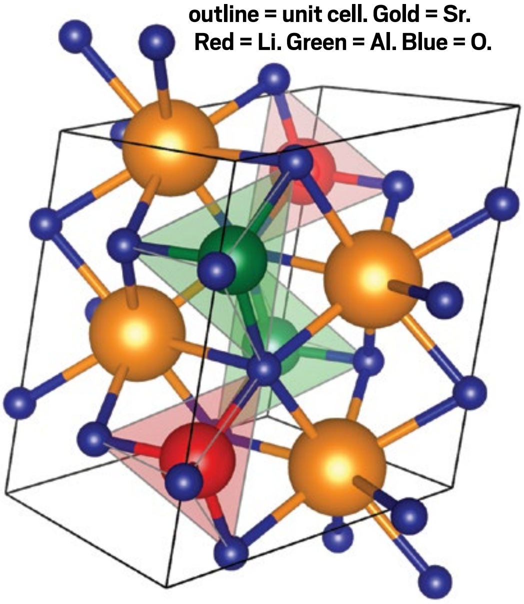
Shining blue light on this Ce^{3+}-doped phosphor powder causes it to emit deep-red light.

CREDIT: C&EN (LED SCHEMES); *CHEM. MATER.* (CRYSTAL STRUCTURE); PHILIPP STROBEL AND CHRISTIAN MAAK/LMU MUNICH (POWDER)

Manufacturers generally opt instead for a simpler and less expensive route, using a blue-emitting LED, indium gallium nitride (InGaN), coupled with a yellow phosphor powder, most commonly an yttrium aluminum garnet (YAG), such as $Y_3Al_5O_{12}$, doped with Ce^{3+}. In this design, referred to as a phosphor-converted LED, the blue light excites the phosphor powder, which is usually encapsulated in the outer casing. The light emitted by the yellow phosphor combines with the blue light emitted by the LED to produce white light.

This single-phosphor design is energy efficient, and the luminescent materials are chemically and thermally stable, according to Christian Maak, who works in Wolfgang Schnick's phosphor research group at Ludwig Maximilian University Munich. But the design is limited to producing light in the cool-white and daylight ranges. And because its output is weak in the red spectral region, it has a low CRI value (less than 75). Those properties make this intense bluish light a popular choice for automobile headlights, for which daylight tones are preferred for visual acuity.

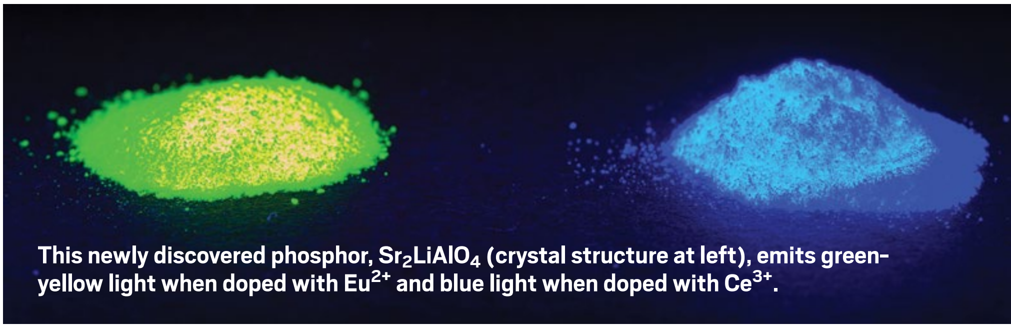
Discovered via computational screening for new phosphors, this compound (below) is the first member of the previously unknown Sr-Li-Al-O crystal family. Black outline = unit cell. Gold = Sr. Red = Li. Green = Al. Blue = O.



For general lighting applications, however, LED makers want warmer colors and higher CRI values (above 80). They have made lights with those properties by blending two or more phosphors and exciting them with LEDs that produce blue or near-ultraviolet light. In all cases, to be commercially viable, the luminescent materials must exhibit chemical and thermal stability and not fade because of constant light exposure. They also need to be inexpensive, abundant, and compatible with standard manufacturing practices. Examples of compounds for multiphosphor LEDs that meet those constraints and are used in high-color-quality LEDs include yellow or yellow-green emitters, such as cerium- or lutetium-doped YAG, and the red-emitting phosphors $(Ba,Sr)_2Si_5N_8$ and $(Ca,Sr)SiAlN_3$, both doped with europium.

Achieving even higher CRI values (above 90), as required by museums, high-end retail stores, and hospital operating rooms, often comes at the expense of a type of energy efficiency known as luminous efficacy. That term quantifies the fraction of light produced within the visible spectrum. Lights that emit radiation outside the range of human vision waste energy.

Most red phosphors boost color quality in white LEDs by filling in red tones, but they also emit broadly, spilling out of the visible spectrum and into the infrared range, wasting energy and causing the light from their LEDs to score poorly in luminous efficacy.



This newly discovered phosphor, Sr_2LiAlO_4 (crystal structure at left), emits green-yellow light when doped with Eu^{2+} and blue light when doped with Ce^{3+}.

Schnick's group reported a breakthrough in that area four years ago. By examining a relatively unexplored family of compounds known as nitridoaluminates, the Munich-based team discovered a strontium member that, when doped with europium ions, functions as a red-emitting phosphor with a narrow emission band (about 50 nm). The sharpness of the emission in the red region means the phosphor produces relatively little infrared light, thereby wasting less energy. The team incorporated the compound, denoted as $Sr[LiAl_3N_4]:Eu^{2+}$, in a prototype LED with a high CRI value and found that it led to an increase of roughly 12% in luminous efficacy compared with commercial high-CRI LEDs (*Nat. Mater.* 2014, DOI: 10.1038/nmat4012).

Schmidt says the nitridoaluminate phosphor, which Lumileds now uses commercially, leads to white-light LEDs with "color rendition that closely approaches that of incandescent lamps—nearly perfect." Yet there is still room for improvement, he says, because a portion of the emission extends into the infrared range.

He notes that if researchers could develop a new phosphor with a narrower emission band shifted slightly toward the orange range, that could lead to an energy efficiency improvement of more than 25%. That advance, which would reduce power requirements and simplify the supporting electronics, could help lower the purchase price of high-CRI white-light LEDs.

Fine-tuning phosphors

The sought-after orange-shifted phosphor hasn't yet made its debut, but other new phosphors with useful properties have hit the scene recently. Earlier this year, for example, Maak and coworkers reported that a family of Ce^{3+}-doped nitridolithosilicates exhibit unprecedented deep-red emission.

"That was a really surprising finding," Maak says, because all other cerium-doped phosphors, which are well known in LED lighting, emit in the blue-to-yellow-orange spectral range (*Chem. Mater.* 2018, DOI: 10.1021/acs.chemmater.8b02604). Because the phosphor's emission spectrum peaks in a sweet spot for photosynthesis, white LEDs incorporating the new material may one day be popular for horticultural lighting applications.

Researchers have also found a new phosphor that seems to outperform those currently used in liquid-crystal displays. LCDs in computer monitors, flat-screen TVs, cell phones, and other gadgets rely on white-light LEDs because they don't generate their own light. Rather, the multilayered LCD structure is generally illuminated from the back via white LEDs.

Electronics companies often create that white light by using the blue emission from a GaN-based chip to excite two phosphors—a green europium-doped compound (β-SiAlON) and a red manganese-doped compound ($K_2SiF_6:Mn^{4+}$).

One hallmark of any high-quality display is its ability to depict a rich assortment of

CREDIT: *JOULE* (CRYSTAL STRUCTURE); SHYUE PING ONG/UC SAN DIEGO (POWDERS)

vibrant colors and hues. Because of the way LCDs create colors, that range—the color gamut—is heavily affected by the individual color components making up the white LED backlight (for example, the green and red from the phosphors and the blue from the source light). In particular, the sharpness of each color component's emission band has a high impact. The sharper the bands, the higher the quality of the LCD output and the broader the color gamut.

At the University of Science & Technology Beijing, phosphor specialist Zhiguo Xia and coworkers recently discovered two related promising compounds for use in LCD backlights. One of them, europium-doped $RbLi(Li_3SiO_4)_2$, emits green light in a narrower band than the reference phosphor, β-SiAlON (*Adv. Mater.* 2018, DOI: 10.1002/adma.201802489). The other compound, europium-doped $RbNa_3(Li_3SiO_4)_4$, emits blue light in an even sharper peak (*Angew. Chem. Int. Ed.* 2018, DOI: 10.1002/anie.201807087).

In LCD tests, an unoptimized white LED backlight made with the new blue phosphor in addition to other components led to a color gamut 75% the size of the industry standard color range—a good start. By combining the new green phosphor with other color components in a white LED backlight, the breadth of the resulting color gamut exceeded the reference color range by 7%.

> "White-light-emitting LEDs are an incredibly promising lighting technology."
>
> **—Joanna McKittrick,** luminescent materials specialist, University of California, San Diego

These phosphors were discovered in the lab, but another new one was found in silico. Efforts to discover new phosphors have nearly always occurred in an Edisonian fashion, through painstaking, trial-and-error experiments—for example, by using exploratory crystal-growth methods and combinatorial chemistry. A new study led by McKittrick and UC San Diego coworker Shyue Ping Ong suggests that computational screening may one day put the kibosh on the lab-intensive approach.

Using density functional theory calculations, the team screened thousands of materials, searching for stable, earth-abundant compounds that could host europium and cerium ions and be excited with blue and near-UV light. The search turned up Sr_2LiAlO_4, the first member of the previously unknown Sr-Li-Al-O crystal family. The researchers synthesized Eu- and Ce-doped versions and found they produced green-yellow and blue emission bands, respectively. Then they used the phosphors to make prototype white LEDs and found they yielded a CRI exceeding 90, suggesting commercial potential for the new low-cost phosphors (*Joule* 2018, DOI: 10.1016/j.joule.2018.01.015).

Computational methods have been used for years to search for new materials for batteries, fuel cells, and catalysts, McKittrick says. But as far as she knows, no one has ever taken this approach to search for new phosphors. "We were astonished by this finding," she says.

Finding a new phosphor using a novel approach may be astonishing. What won't be astonishing, however, is if in the next few years, LEDs take over the lighting world. Just watch and see, McKittrick says. "White-light-emitting LEDs are an incredibly promising lighting technology." ■