Storage Phosphors Could Replace Electrically Powered Lighting

Sunlight can be stored as electron-hole pairs and then used at will. We need to understand the benefits and pursue the technology

By Geoff Graham September 1, 2022

Questions? Comments? Anything left out? Anything you disagree with? I'd love to hear your thoughts. Email me at gjgraham4health@protonmail.com.

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Summary

Humanity benefits enormously from artificial lighting. Consequently, the use of artificial lighting is likely to increase greatly. However, artificial lighting increases CO2 emissions at a time when reducing such emissions is imperative. Artificial lights powered by solar-generated electricity (photovoltaics) might limit CO2 emissions, but solar-generated electricity is expensive and prone to performance losses.

In this article, I argue that phosphors, materials that absorb and later reemit photons, might replace other artificial lighting, particularly in places where labor is plentiful and capital is scarce. Among phosphors, the "storage phosphor" subclass, whose members save their energy until it is summoned by its user, would be the most valuable.

Storage phosphors are portable. They can be loaded with energy ("charged") in one location and unloaded ("discharged") somewhere else. As this article explains, they might be charged above the clouds on overcast days, and thus avoid a key weakness of most types of solar electricity.

For storage phosphors to be useful, users must be able to stimulate them to emit light in a controlled manner. Promising stimuli include electric current, electric fields, high-energy photons, mechanical force and heat.

Phosphors, including storage phosphors, can be divided into 3 categories. These are inorganic phosphors, organic (carbon-based) phosphors, and biological phosphors.

Inorganic phosphors are currently the most advanced type of phosphor; at least one inorganic phosphor has achieved continuous phosphorescence of 360 hours. However, inorganic phosphors are difficult to work with and typically depend on scarce and very expensive exotic metals.

Organic (carbon-based) phosphors have achieved continuous phosphorescence of 20-40 minutes. They are cheaper than inorganic phosphors and more malleable. They include a number of promising approaches, one of which is to exploit the properties of polymers. In an important advance, an inorganic phosphor was created that is capable of "upconversion", the emission of photons that are more energetic than the incident photons.

Biological materials also phosphoresce and might become the basis of storage phosphors. Biological materials have the disadvantage of fragility, but the advantages of existing in an enormous number of varieties and of being easy to produce in large amounts.

Phosphors are valuable in medicine and biomedical research, and in anti-counterfeiting efforts, information storage, and passive night lighting. This ensures that research into phosphors will continue. However, public awareness of the potential benefits of sunshine storage phosphors could increase the intensity of that research and ensure that research that is especially valuable to sunshine phosphors (e.g., research leading to high-volume production) is not overlooked.

Investors should regard this as an established, but growing technology being put to a new purpose.

Note about the cited references: Reference indicators are in the form "[A1]". These indicators are hyperlinked directly to the cited reference. However, the references are also listed at the bottom of this article. Most of these listed references also include an entry such as this: "M: Lighting accounts for 15 percent." The red-colored text is a text string that occurs exactly once in the cited reference and marks the region in the reference where the cited information is present.

A. The environmental cost of adequate lighting. The production of light accounts for about 15% of global electricity consumption and 5% of global

greenhouse gas emissions. At the same time, 1.2 billion people lack access to modern energy services, including reliable lighting. For many people, hazardous energy sources such as kerosene are the only option [A1]

Efforts to improve this situation have focused on providing high-quality lighting fixtures and efficient light bulbs such as Light-Emitting Diode (LED) bulbs to millions of people [A2]. However, even efficient light bulbs require electricity, which must be provided somehow.

B. The limitations of photovoltaics. Photovoltaic electricity generation is expensive. In the United States, after solar tax credits, the cost for a solar panel system on an average-size house ranges from \$11,144 to \$14,696, according to EnergySage. A person who needs s few panels for a Do-It-Yourself project can expect to pay \$200-\$250 per panel (about \$1 per watt) [B1].

Most solar photovoltaic panels have an efficiency of between 11% and 15% [B2]. Solar energy-powered lighting systems also include lithium-ion batteries and LED bulbs. Reliable information on the real efficiencies of lithium-ion batteries and LED bulbs is difficult to find on the Internet, but a 2017 study from Germany found a round-trip efficiency of lithium ion batteries to be 70-80% [B3]. The theoretical maximum efficiency of LED bulbs is around 390 lumens per watt [B4] while real LED bulbs deliver at best about 120 lumens per watt (about 30% efficiency) [B5]. Hence, artificial lighting powered by solar electricity may be as little as 4% efficient, overall.

No recapture of room light. Much of the light emitted by indoor lighting fixtures falls upon walls and ceilings, and thus might be subject to recapture. However, no attempt is made to do this, presumably because the efficiency of photovoltaic systems is so low.

Loss of performance. The performance of solar panels may deteriorate. When a panel's energy cannot flow to the system's inverter (which transforms direct current to alternating current, i.e., $DC \rightarrow AC$) the panel becomes overloaded and gets hot. Hot spots can reduce a solar panel's performance and lifespan and, in some cases, can damage it beyond repair [B6].

In addition, the buildup of moisture within a solar voltaic system can create "snail trails" which decrease the system's performance. [B7].

C. Continuous phosphors and storage phosphors. Materials that can store the energy from light and later release that energy as light are another option.

Luminescence is the spontaneous emission of light by a material where the light

energy is not created by heat. (If the energy of the emitted light is created by heat, the process is called "incandescence"). [C1] [C2]

Photoluminescence. Photoluminescence is light emitted from a material after the material has absorbed photons [C3]. Electrons in the material are excited by the photons into an energy level that is higher than their ground state. Later, an excited electron returns to its ground state and emits a photon in the process. When an electron is excited to a higher state of higher energy, it leaves behind a "hole" with which either the electron or another excited electron can "recombine" and emit a photon while doing so [C4]. Recombination of electrons and holes is discussed here [C5].

Fluorescence is light emission that ceases within about 10 nanoseconds after the cessation of the incident light [C6].

Phosphorescence is light emission that continues more than 10 nanoseconds or longer (up to 360 hours or more [C7]) after the stopping of incident light.

Continuous phosphorescence is my term for phosphorescence that begins when electrons in the material are excited by incident light and continues until the store of excited electrons is exhausted. Continuous phosphorescence is sometimes referred to as "persistent luminescence." [C8]

Storage phosphors are materials that store light as excited electrons, but which do not emit that light until induced to by some stimulus [C9]. It is possible for a material to display continuous phosphorescence and storage phosphorescence at the same time [C10].

Forbidden transitions. In phosphorescence, emission of a photon requires an excited electron to move downward via a "forbidden" (highly improbable) transition. The improbability of this transition accounts for the delay in light emission. A simple, but good, explanation of phosphorescence is given here [C11].

Electrons, holes, and lattice defects. Another type of phosphorescence occurs when an incoming photon dislodges an electron into a defect in the lattice of a crystalline or amorphous solid [C12]. Eventually, this trapped electron may be released by a random spike of thermal (vibrational) energy or by some other influence. The released electron may then emit a photon as it transitions to a low-energy state in an atom of the material. In some cases, this lower-energy state may be a "hole", i.e., an atom in the lattice from which an electron has been removed and not replaced.

The experts who study this type of phosphorescence believe that holes can also be trapped within lattice defects and then released. Since holes are the absence of an electron, it may seem odd that something that is not present can somehow be

trapped. However, as an analogy, if one covers a 64-square checkerboard with 63 checkers, each on one square, with only one square having no checker, the missing "hole" can be moved around on the checkerboard surface just as though it were a real object. Trapped electrons and trapped holes are discussed here [C13] [C14] [C15].

In the scientific literature, delayed emission of light caused by a forbidden electronic transition is often referred to as "phosphorescence" and delayed emission caused by trapping of electrons or holes is often referred to as "persistent luminescence." However, for simplicity, in this article, both types of delayed photon emission—whether from forbidden electronic transitions or electron/hole escape from traps—are referred to as "phosphorescence."

Continuous phosphors vs. Storage Phosphors. Trapped electrons may be released slowly by vibrations caused by the ambient temperature or, if they are in a "deep trap" they may remain trapped until and unless some more energetic circumstance releases them. Materials containing trapped electrons that are slowly released by ambient temperature are continuous phosphors. Materials containing electrons in deeper traps that resist ambient temperature are storage phosphors [C16]. As noted above, a given material can be both a continuous phosphor and a storage phosphor [C17]. Moreover, a storage phosphor that is heated to a high enough temperature will become a continuous phosphor.

Controlled emission of light. Although ambient temperature is insufficient to release electrons from deep traps, more powerful influences can do so, which means that luminescence from storage phosphors can be controlled. The stimulus that releases electrons from deep traps, promoting their recombination with holes and the emission of light, can consist of light, pressure, heat, or possibly an electric field [C18] [C19].

Storage phosphors are more useful. Although both continuous phosphors and storage phosphors can be useful in storing light for later use, storage phosphors are the more useful of the two since no light is lost from the storage phosphor until light from it is summoned.

Phosphor emission color is tunable. In general, phosphors are tunable in their color emission, with many different colors achievable. These colors include cold white, standard white and warm white, which are most useful for indoor and outdoor lighting [C20] [C21] [I9].

Transparent electrodes. Generation of an electric current or an electric field requires the use of electrodes. If stored luminescent energy is to be released by electric current or an electric field, at least one electrode must be transparent in

order to allow the emitted light to escape. A common solution is to use glass coated with indium tin oxide as the transparent electrode; if the light-generating material is a thin layer, the back electrode can be coated with reflective metal. Other materials that can be used as the transparent conducting electrode include carbon nanotubes and PEDOT (Poly(3,4-ethylenedioxythiophene) [C22] [C23]

Resistance to heat quenching. Heat can release trapped electrons, preventing their use for illumination (this process is called "heat quenching") and direct sunlight can heat materials to high temperatures. Hence, for a storage phosphor to be useful, it must resist heat quenching at temperatures that sunlight can create. Fortunately, this seems to be possible: in at least one storage phosphor, there is no heat quenching up to 600 K (327 °C). [C24].

D. Advantages and disadvantages of phosphors. Storage phosphors have advantages and disadvantages as methods to replace electrically generated lighting.

Harvesting and distribution of emitted light. Imagine that after dark, a family of three wishes to use some of the light saved up during the previous day. The house has a walkway to the front porch, with a lamp at the beginning of the walkway and another lamp on the porch. One parent is cooking in the kitchen and has several lights on. The one child is studying at a desk, with both the bedroom light and a desk lamp on. The second parent is working on the back patio, which is also illuminated by outdoor lights. How can enough light be harvested during the day to cover these needs, and how can it be liberated and distributed properly at night?

Harvesting of adequate amounts of sunlight would probably require the exposure of multiple large-area storage phosphor panels during the day in succession, with each panel being replaced with another after it became saturated with light. This could presumably be done robotically, but the process would require electrical energy, which offsets the value of the storage phosphors in saving electricity. It might be done manually in regions with abundant labor.

The process of liberating and distributing stored light from a phosphor would require a means to induce photoluminescence from multiple patches of activated storage phosphor in succession. Moreover, it would require optical fibers and a switching system to distribute the emitted light to desired locations within the house. As of today, the switching system would have to be mechanical, but there is reason to believe that a magnetic system with no moving parts could be devised [D1]. Optical fibers are not 100% efficient in transmitting light and this would lower the system efficiency.

Portability. One big advantage of storage phosphors is that they are portable, both before and after they have absorbed photonic energy. For example, it might be

possible to expose storage phosphors to sunlight on the grounds of a sports stadium and then use the charged phosphors to light the stadium at night or to transport the charged phosphors to people's houses.

Aerial charging of phosphors? It might also be possible to transport storage phosphors to a high altitude using a tethered balloon. This might be done in order to raise the phosphors above a cloud layer and into direct sunlight or might be done to avoid the "visual pollution" of having phosphors scattered around the landscape while they were being charged. If the purpose was to avoid visual pollution, the balloons and the tethers might be painted blue to blend in with the sky.

The US government possesses several Tethered Aerostat Radar Systems (TARS) that can rise to an altitude of 15,000 feet while tethered to the ground. The largest of these can lift a 1000-kilogram payload [D2]. A similar system, perhaps using hydrogen rather than helium balloons, might be used to expose storage phosphors to sunlight above the clouds. A lightweight storage phosphor that could be rolled up and unrolled like a gigantic roll of wax paper might absorb enough sunlight to make the scheme worthwhile (no such phosphor exists, yet). If done on a large scale, this would pose a hazard to aerial navigation which would have to be accounted for and controlled. Moreover, phosphors containing large amounts of stored energy would create a danger of fire, and perhaps explosion.

Favored geographic areas. Phosphor-based lighting might be suited for areas where unemployment is high, labor is inexpensive, capital is scarce and other lighting technology is absent. In such circumstances, manual labor could be used to keep the panels dry and dust-free, to harvest them after peak sunlight, and to load them into machines that can liberate the stored light in a controlled fashion.

Could interior light be recycled? Although sunlight is likely to be the main source of energy to charge storage phosphors, interior light might also be captured and reused. Most interior light falls upon walls and ceilings. Some storage phosphors are capable of "upconversion", which is the combining of low energy photons to boost electrons into a high energy levels. When these high-energy electrons discharge, they create high-energy photons. Upconversion might allow infrared light to be captured and reemitted as visible light. Note, however, that photons that are captured by the walls or ceiling of a room will not be reflected, and thus will not contribute to the room's illumination.

E. The protection of storage phosphor panels. As with all technology that harvests sunlight, solar energy phosphors would have to be shielded from dust, precipitation, bird droppings, and so on. A transparent protective barrier would be

necessary. Such a barrier would likely be composed of either glass or plastic, each of which has advantages and disadvantages.

Clear plastic barriers. A vendor named TOPAS, and perhaps other vendors as well, sells clear plastic barriers that are designed to transmit as much ultraviolet as possible over a range that ends at the high-energy wavelength of 220 nanometers. However, this plastic has no stabilizers against ultraviolet light damage and so will degrade after long exposure to ultraviolet light. The plastic is unaffected by moisture or heat up to 170 °C, which suggests that it will not overheat in direct sunlight. [E1].

Glass barriers. The UV transmission of several types of glass was measured. All tested glasses blocked wavelengths shorter than 315 nanometers. Smooth ordinary glass was the best transmitter of ultraviolet A (320 to 400 nanometers); it transmitted about three-quarters of incident ultraviolet-A. [E2]. Thus, glass transmits less light than does the TOPAS plastic, but is likely to be much more durable.

The benefits of ultraviolet light. Transmission by plastic or glass of ultraviolet (UV) light increases the effectiveness of sunlight phosphors since high-energy UV wavelengths should efficiently dislodge electrons into higher-energy states [E3]. UV radiation is present in sunlight and constitutes about 8% of the total electromagnetic radiation output from the Sun, although much of this is screened out by Earth's atmosphere, with the amount screened out depending on circumstances [E4] [E5].

F. The stimulation of photoemission. As explained above, energy stored in a continuous phosphor is released continuously at ordinary ambient temperature because the vibrations induced in the material are adequate to dislodge high-energy electrons from their traps. However, excited electrons stored in a storage phosphor cannot be dislodged in that way. If the energy in such electrons is to be used productively, the excited electrons must be dislodged by some controlled influence.

Heat induction of photoemission. Heat can induce photoemission, as mentioned above. A short burst of heat might be used to discharge the stored light in a storage phosphor. The heat would have to be mild enough not to damage the storage phosphor over many cycles. Concentrated bright sunlight might supply heat to a reservoir that could be used to release trapped electrons or holes, but this seems less likely to succeed in winter or on cloudy days. Release of trapped

luminescence by heat is called thermoluminescence. An example of controlled thermoluminescence is given here [F1].

Piezoelectricity can stimulate photoemission. Piezoelectric charge can induce charge-hole recombination. The piezoelectric effect is the ability of certain materials to generate an electric charge in response to applied mechanical stress. Strictly speaking piezoelectricity is generated when the material deforms elastically but does not fracture or rupture chemical bonds (which is "fractoluminescence) [F2]. The use of piezoelectricity to dislodge trapped electrons and create luminescence is called piezoluminescence [F3]. The creation by gamma rays of trapped electrons in crystals of lithium fluoride and other compounds, followed by photoemission caused by the application of pressure is an example of this [F4]

Light itself can stimulate photoemission. In addition to exciting electrons to higher energy levels, light can dislodge those electrons from their traps. The use of light (including laser light) to dislodge electrons and create luminescence is called photostimulated luminescence [F5] [F6].

Laser release of trapped luminescence. Light-luminescence properties were also used to developed data storage devices. Recently, Xie et al. fabricated flexible phosphor films by encapsulating a series of deep-trap storage phosphors with multicolor emissions into silica gel. Information was conveniently encoded to the film using a 405-nm laser and the decoding process was conducted by scanning with a 980-nm laser. [F7]

Self-stimulation of emission? It might be possible to induce a small portion (say 10%) of stored light from a patch of storage phosphor and use that light to induce the remainder of the stored light. This might require upconversion (see Section G, below) of the starter-induced light.

Electric fields or currents? The most convenient way to liberate trapped electrons and holes in a storage phosphor would be to apply an electric field or electric current—if doing so would succeed. I would guess that a brief, high-voltage-low-current electric field would be most effective.

Society has an enormous amount of experience with electroluminescence, in which a material emits light in response to the passage of an electric current or to a strong electric field [F8]. Society also has much experience with television phosphors, in which high-energy electrons, accelerated by a strong electric field, create excited electrons and holes, which recombine to emit light [F9]

Despite the above, it is difficult to find evidence on the Internet that either an electric current or an electric field will liberate trapped electrons in a storage

phosphor. If they do not, then it might be possible to incorporate ordinary electroluminescent material into storage phosphors such that a brief current could stimulate electroluminescent light emission, which would then stimulate phosphorescence of trapped electrons. As noted above, transparent electrodes may be necessary to allow emitted light to escape but are easy to manufacture [F10]

None of the above methods of stimulating the emission of light from storage phosphors will be worthwhile unless the amount of light liberated is much greater than the amount that could be generated by the stimulation signal itself. Maximizing the ratio of light emitted to energy expended in stimulation may be the greatest challenge.

G. Upconversion. An important property of some phosphors is their ability to "upconvert" some of the solar radiation that strikes them. Almost half of sunlight consists of invisible infrared frequencies that would be wasted if phosphors could only re-emit those frequencies at the same or longer wavelengths [G1]. This problem is exacerbated by the fact that trapped electrons can lose energy non-radiatively, by increasing the vibrational energy of atoms that they contact or by "tunneling" toward lower energy levels [G2].

Upconversion defined. Photon upconversion is a process in which the sequential absorption of two or more photons leads to the emission of light at shorter wavelength than the excitation wavelength [G3]. An example is the conversion of infrared light to visible light. [G4] [G5].

H. Incentives to further research. Technological development proceeds fastest when modest investments of time and money toward research produce commensurate financial rewards and when there is a long series of rewarding goals to achieve, each building upon previous achievements. (This may be a reason why cybernetics and electronic communication have progressed so rapidly, but progress toward controlled nuclear fusion has been much slower. It is hard to convince legislators or private investors to put \$50 billion dollars into a device that will raise the progress toward ignition from half-way to two-thirds but provide no other benefit.)

Fortunately, phosphors have commercial uses that are valuable, but which could be improved. The pursuit of more effective and cheaper ways to fulfil those commercial uses is likely to motivate additional research.

Night lighting. Several continuous phosphors have been commercialized as night-vision materials. They show strong luminescence for more than 10 hours. They can be excited by sunlight or room light. It seems reasonable that users would want materials that absorb and re-radiate more light, emit light over a longer period, are cheaper, are more durable, and emit light of a desired color (usually white). Hence, research on this use of phosphors is likely to continue [H1]

Anti-counterfeiting technology. Storage phosphors can be used as an easy method to detect counterfeiting of artwork, cheques, merchandise, medicines, and so on. The strategy is to affix to each authentic item, at the time of manufacture, a storage phosphor with a trademark or serial number attached to it. The message might appear as a luminous signal that would last for a minute or so, after exposure to some inducing influence such as heat or mechanical pressure. Successful counterfeiters would have to duplicate both the storage phosphor and the trademark or serial number. The contribution of phosphors to anti-counterfeiting efforts is discussed here [H2].

Further research might improve anti-counterfeiting measures by creating storage phosphor that produced a pattern of light at an exact wavelength of color or a group of monochrome colors that could be checked by an analytical device or perhaps a cell phone.

Information storage. Luminescing materials can be used for information storage [H3]. Photons are useful carriers of information: they travel rapidly, and it is possible to detect even a single photon [H4]. Moreover, recent work suggests a non-mechanical method of controlling photon flow between alternate paths [H5]. Hence, photons may play a much larger role in cybernetics in the future, and this favors more research on phosphors.

Biomedical applications. Biomedicine is probably the field with the greatest potential for near-term expansion of phosphor technology because of phosphors' usefulness in imaging. Fluorescent tags allow doctors and researchers to illuminate tissues, guide surgery, track implanted microdevices, track injected medicines [H6] [H7], and even track individual cells. However, if the fluorescent tags must be irradiated at the same time that they are imaged, the irradiation can cause surrounding tissues to fluoresce ("autofluorescence"), greatly decreasing the signal-to-noise ratio [H8]. Furthermore, irradiation of tissues with ultraviolet light can damage those tissues. Hence, the delay between electron excitation and light generation by continuous phosphors is very valuable to medical imaging.

Continuous phosphors have been made into nanoparticles, that can be injected into individual cells. Such cells can then be tracked in *in vitro* experiments or in experimental animals. [H9]

Fluorescent mesoporous silica delivered doxorubicin. Doxorubicin-loaded ZGO@SiO2 potently inhibited the growth of U87MG cells (human malignant glioma) in vitro when compared to an unloaded control. Since the carrier of the doxorubicin (ZGO@SiO2) is also a continuous phosphor, it could be tracked in vitro. [H10] [H11].

Biosensing of tumor cells. Continuous phosphors were attached to gold particles that were attached to an antibody to α -fetoprotein. The purpose was to identify tumor cells that inappropriately express α -fetoprotein [H12].

I. Inorganic vs organic phosphors. Phosphors can be divided into two groups: inorganic and organic. Each has advantages and disadvantages. Briefly, inorganic phosphors can emit light for much longer periods of time, but contain rare and expensive elements, and are difficult to engineer. Inorganic-organic hybrid materials are also under investigation.

Inorganic phosphors are more advanced but more expensive. Inorganic phosphors doped with rare-earth elements exhibit excellent optical performance with long photoemission times, and they are durable. However, they require a complex fabrication process and some injure living tissues, which limits their medical use and thereby lessens their prospects for further development.

The high cost of inorganic phosphors. If storage phosphors are to contribute significantly to global lighting, storage phosphor panels will have to be deployed in large numbers. A very serious constraint on the number of inorganic storage phosphor panels that can be deployed is the cost and scarcity of some of the metals used.

Y₃ Al₂ Ga₃ O₁₂: Tb³⁺ is a promising phosphor [II] that includes expensive elements. Although yttrium (Y), aluminum (Al) and oxygen (O) are fairly cheap, terbium (Tb) costs \$4085 per kg (as of this writing) and gallium (Ga) costa about \$470 per kg.

Another prominent luminescent material, SrAl₂O₄:Eu²⁺-Dy³⁺, includes europium (\$7500 per kg) and dysprosium (\$220 per kg). [I2]

Yet another phosphor, Zn₃Ga₂Ge₂O₁₀:Cr³⁺ [I3] includes both gallium (Ga, \$470 per kg) and germanium (Ge, \$1200 per kg. [I4]).

The storage phosphor Y₃Al₂Ga₃O₁₂, which can be doped with Ce3+ and Cr3+, [15] is less expensive than the examples above, but contains gallium (Ga), at a cost of ~\$470 per kg.

Advantages of organic phosphors. Compared with inorganic phosphors, organic phosphors are easier and cheaper to produce. It is easier to alter their chemistry by attaching functional organic groups and biological ligands [16]. However, it is still difficult to design organic materials that emit light persistently. The persistence has increased from milliseconds to seconds [17] and then to 20-40 minutes [18], but this is still short of the many hours that inorganic emitters can persist. Recently a simple organic persistent luminescent material was described that can be doped to provide cold white, standard white or warm white light (as well as cyan) [19].

J. The chemistry of phosphors. The chemistry that enables phosphors to exist is beginning to yield its secrets.

Typical inorganic formulas. Chemical formulas for inorganic persistent luminescence materials and storage phosphors follow a pattern. They include 2 or 3 types of metal ion and between 1 and 5 atoms of each type of metal. Several oxidizing atoms are present; usually, these are oxygen, but they may be something else, such as fluorine. To this background are added doping atoms which are always transition metals or rare earth metals.

 $Examples\ are\ Y_3Al_2Ga_3O_{12}:Tb^{3+},\ Y_3Al_2Ga_3O_{12}:Cr3^+,\ SrAl_2O4:Eu2+-Dy3^+,\ SrAl_2O_4:Eu^{2+},Dy^{3+},\ CaAl_2O_4:Eu^{2+}Nd^{3+},\ Y^2O^2S:Eu^{3+},Mg^{2+},Ti^{2+},\ Zn_3Ga_2Ge_2O_{10}:Cr^{3+},\ ZnGa_2O_4:Cr^{3+},\ LiGa_5O_8:Cr^{3+},\ Ca_3Ga_2Ge_3O_{12}:\ Nd^{3+},Cr^{3+},\ NaYF_4:25\%Yb,\ 0.5\%Tm.$

Rigid cages needed. One important constraint on the composition of inorganic phosphors is the need to create rigid molecular cages for trapped electrons. Because trapped high-energy electrons can lose their energy by increasing the vibration of the atoms around them, rigid molecular cages are required. Non-radiative relaxation is the biggest competitor to radiative relaxation. This arrangement is sometimes called the "hosts-guests" system. [J1].

Promotion of "forbidden" transitions. Inorganic delayed emitters must promote energy level transmissions that are of the "forbidden" type to preserve the ability of trapped electrons to emit photons [J2] [J3]

Additive coloration of luminescence. Inorganic phosphors can emit light in various colors. Careful choice of groups of phosphors, or manipulation of multiple doping elements, can allow engineers to manipulate the color of the emitted light. Since white light is usually the desired color this requires red, green, and blue light

in proper proportions. One combination of emitters that can produce this result includes the green emitter SrAl₂O₄:Eu²⁺,Dy³⁺, the blue emitter CaAl₂O₄:Eu²⁺Nd³⁺, and the red emitter: Y₂O₂S:Eu³⁺,Mg²⁺,Ti²⁺ [J4] [J5].

Forster Resonance Energy Transfer. Forster Resonance Energy Transfer (FRET) is a process by which energy can be transferred between two color-producing compounds that are in very close proximity [J6]. The basis of FRET is well understood, and FRET can be used to modulate the colors of delayed emitters [J7] [J8].

Organic delayed emitters. Organic (carbon-based) delayed emitters have, as mentioned above, much shorter durations of emission than do inorganic delayed emitters. However, recent work shows that a phosphor can be created from a strong electron donor N,N,N',N'-tetramethylbenzidine and a strong electron acceptor 2,8-bis(diphenylphosphoryl)dibenzo[b,d]thiophene. These achieved luminescence of about 1 hour [J9].

Polymeric phosphors. Polymers, whether composed of just one type of monomer or more than one, can also be used to engineer phosphors. Owing to the long π -conjugation conducting bands of some polymers, energy can be stored in the semiconducting layer. One example emitted near infrared for 1 hour after excitation by white light [J10].

Multi-component polymers. A number of organic monomers are suitable for polymerization into phosphors and can be mixed to form multi-component continuous phosphors. The resulting polymers have excellent mechanical flexibility. However, the length of detectable emissions is so far about 7 minutes [J11]

Other promising chemistries. Metal-Organic Frameworks have a rigid inorganic porous structure which can capture and stabilize emitter molecules, preventing them from dissipating their excitation energy non-radiatively [J12].

Zn-isophthalic acid is another promising system which produces tunable (green, red, cyan, yellow) luminescence. However, it has reached a period of luminescence of only 22.4 seconds [J13].

K. Could biological materials beget storage phosphors? Biological materials phosphoresce (explained below), which suggests that biological materials might give rise to storage phosphors. The biological materials might themselves become the storage phosphors, or they might serve as a model for the construction of storage phosphors from non-biological materials.

The advantages of biological materials as storage phosphor candidates.

There is an enormous variety of biological materials in the world, and this variety can be increased by controlled mutagenesis. Screening candidate materials for light emission is easy. If the biological materials were themselves the storage phosphor materials, rather than a molecular model for them, large amounts of storage phosphor material might be produced inexpensively.

The disadvantages of biological materials as storage phosphor candidates. Most biological materials, such as proteins and biochemicals, are not durable and do not resist exposure to the environment. Thus, they are more likely to serve as molecular models for storage phosphors than as the actual material, but this would require more research and might fail.

A major complication in screening biological materials for light-induced phosphorescence is that many biological materials emit light through the process of chemiluminescence. Measures would be needed to prevent confusion between the two processes.

A circumstance that is both an advantage and a disadvantage is that little or no research has been done on biological materials as storage phosphors. This means that researchers would be starting almost from zero, but it has the advantage that any discoveries they made would probably not be the intellectual property of someone.

Examples of phosphorescence in biological materials. Many human tissues autofluoresce under UV or other light. As mentioned above, this is a major motive for the development of phosphors for medical use. Autofluorescence of tissues is used to diagnose a number of human diseases [K1]. Hence, many living tissues, from humans and presumably other species, can reemit incident light.

Some calcified human tissues, under some circumstances, can phosphoresce (reemit incident light after a delay of a few microseconds or more). In one study, for human dentine, bone and enamel the experimental lifetimes of phosphorescence were 31 ± 2 sec [K2].

A different study showed that human bone samples heated to at least 400 °C phosphoresce. Maximum phosphorescence occurred in human bone samples heated to 700 °C [K3].

Identification of phosphorescing molecules in tissues. Attempts to identify the light reemitting molecules in biological tissues have implicated specific proteins (collagen, elastin, keratin, etc.) and various non-protein biochemicals [K4]. Three amino acids—tryptophan, tyrosine, and to some extent phenylalanine—contribute to the fluorescence and phosphorescence of proteins

[K5] [K6]. The contribution of tyrosine depends largely on a protein's folded state [K7].

Collagen has been reported to be the main source of autofluorescence of bone tissue [K8], and phosphorescence of calcified tissues apparently stems principally from the organic moiety [K9]. However, phosphorescence of bone tissue occurs at temperatures (700-800 °C) at which the organic component of bones must surely either be greatly altered or absent, suggesting that the mineral component of bone is the cause [K10]

Screening microbes and other organisms for phosphorescence. There exists very sensitive equipment that can detect and record light emission. Researchers searching for phosphorescence could screen collections of different microbes or other organisms, or they could screen multiple mutants of a single species, or they could fractionate and screen the components of a single organism or clone.

If I were doing the screening, I would keep track of the phosphorescence intensities of various candidates, but also of the duration/intensity ratio. This latter could correct for differences in total mass of the individual colonies and for the concentration of the phosphorescent component(s) within individual organisms. Candidates with a high duration/intensity ratio would be considered more promising.

Biological materials under abnormal conditions. It appears that ordinary biological conditions frequently quench phosphorescence that might otherwise lead to something useful. The most interesting study along this line showed that three-quarters of the (at least) 25 proteins tested had light-induced phosphorescence times of between 500 microseconds and 2 seconds, and that nearly all proteins display phosphorescence of at least 30 microseconds. However, dissolved oxygen in the medium containing the proteins had a very strong quenching effect on protein fluorescence [K11].

This study also showed that isolation of the indole ring of tryptophan from the solvent increased the duration of phosphorescence [K12]. In addition, the study showed that addition of calcium to the calcium-binding protein parvalbumin increases the duration of phosphorescence by at least five-fold, presumably by limiting the fluorescent moiety's exposure to solvent [K13]. Replacement of the H2O in the solvent by deuterated D2O had a similar effect [K14].

An earlier study by different authors [K15] showed that at cryogenic (liquid nitrogen or dry ice) temperatures proteins typically phosphoresce for 3 seconds or longer. Presumably, the low temperatures prevented quenching of the phosphorescence by solvent or oxygen.

These results suggest that proteins in unnatural circumstances, such as dried proteins protected from oxygen, might phosphoresce for long periods after illumination. Unfortunately, screening for such proteins is likely to be haphazard and laborious unless a clear picture of protein phosphorescence can be developed.

Prospects for a biological storage phosphor. Although biological materials with long-duration continuous phosphorescence might be useful, the most valuable prize is the storage phosphor composed of biological material. As noted above, a storage phosphor stores incident light energy as excited electrons but relinquishes that energy as photons only upon some stimulus, and hence is subject to control. As discussed above, the stimulus might take the form of heat, electric current, an electric field, light energy, mechanical pressure, and perhaps magnetism.

To my knowledge, there is no published research on this subject. However, the presence of a biological storage phosphor might confer a Darwinian advantage on an organism. A storage phosphor could record the most recent exposure to sunlight. If the excited electrons in the phosphor slowly decayed radiatively or non-radiatively, and if the organism could perceive the decay, the storage phosphor might regulate the organism's metabolism or behavior in response to sunshine.

L. What needs to be done. In order to use storage phosphors and persistent luminescence materials in lighting, we need further research to improve their properties. The most important objective is to increase both the brightness and the duration of emitted light. Controlled emission of strong light for one minute from a storage phosphor has been documented, but more absorption of light and more efficient storage of that light are still needed [L1]

American researchers should note that almost all recent publications on phosphors have been authored in China. Western scientists should be grateful to China for sharing its results, but the USA needs to reverse our habit of falling behind in economically and strategically important technologies.

Use of storage phosphors to replace standard artificial lighting could prevent emission of large amounts of CO2 into Earth's atmosphere and perhaps forestall harsher CO2 emission-control measures.

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Note: The red text strings below in this format: "M: Lighting accounts for 15 percent" are unique within the published reference and can be used to search for the referenced information.

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