

Light Activated Persistent Phosphorescence

Materials, Applications, Science



Figure 1. Copper-activated ZnS afterglow at 530 nm. Application limiting drawbacks include sensitivity to moisture over time and short afterglow time and rapid decrease in intensity after only a few hours. Enhancement of afterglow intensity by incorporation of a large amount of dopant (activator) negatively affects both mechanical and physical properties leading to a rapid degradation in chemical stability.

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Historical awareness

The term phosphorescence is usually attached to luminous materials or substances at ambient temperature that glow without any obvious light emitting mechanism or intrinsic energetic light source. As such, they have historically been imbued with a somewhat magical quality. More recently, science has provided general insight into the processes responsible for this phenomenon but in many cases, although there is agreement on the general theory, the mechanistic details for different examples have yet to be precisely worked

out and the subject remains an area of active investigation, discovery, elucidation and application.

It is reported that examples of persistent phosphorescence were observed over 2000 years ago in particular Chinese paintings that remained visible at night as a result of incorporation of certain substances. More recently, from about 1500 on, there have been records of minerals that showed luminous characteristics after being exposed to sunlight. One of the terms for this phenomenon, luminescence--sometimes today used interchangeably with phosphorescence,

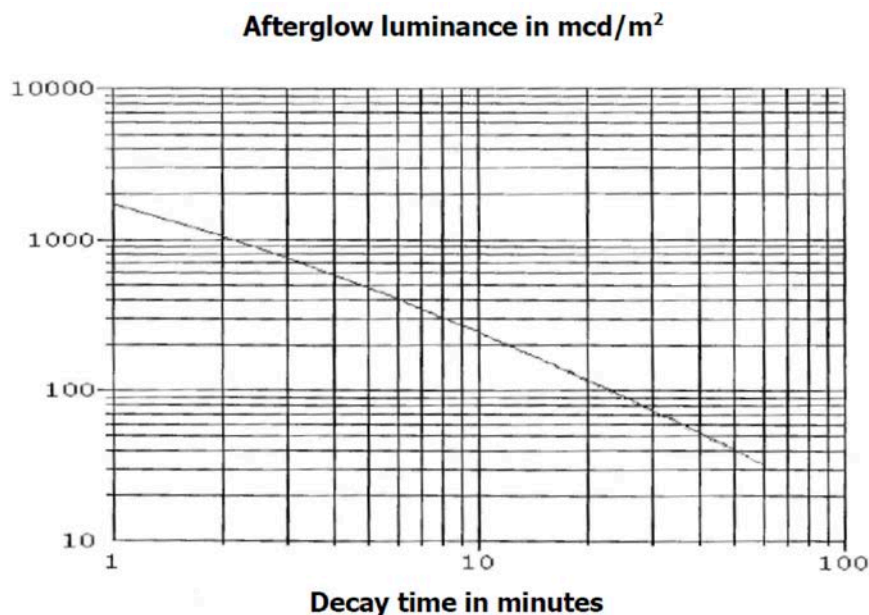
was coined by Eilhardt Wiedemann in 1888 as a term to refer to “light without heat.” Phosphorescence is only one of several light emitting processes addressed under this heading and persistent phosphorescence is an example of materials capable of time-extended light emission after excitation.

Zinc Sulfide (ZnS)--first modern generation of persistent phosphors

Discovery and deployment of the first generation of persistent phosphors began in the late 19th century with the recognition of the photoluminescence of zinc sulfide (ZNS). During the early part of the 20th century an investigator by the name of Lenard found that the addition of specific metal impurities such as copper (Cu) or silver (Ag) to ZnS could enhance its ability to phosphoresce at a specific wavelength of visible light after being exposed to sunlight. For this reason he termed these impurities activators. Today, the term “dopant”, used in far wider application, has supplanted “activator” and refers not only to applications in creating or enhancing luminescent phosphors but a standard component in the activation of materials deployed in modern semiconductors that underpin the circuitry of computers, optoelectronic devices, telecommunications and much more.

During a good part of the 20th century, interest in and applications of doped ZnS phosphors took separate developmental directions. One set, along with semiconductor development, included electrically driven optoelectronic applications such as flat panel displays, cathode ray tubes, fluorescent lamps and illuminated traffic signals. Passive applications, with which this article is concerned, includes both novelty and decorative uses on the one hand and self-luminous safety and directional signage on the other. One specialty area still popular today is the use of ZnS phosphors in luminescent watch dials for military applications. Initially both radium and tritium were employed as activators but these

Figure 2. Afterglow characteristics of SrAl₂O₄:Eu²⁺, Dy³⁺ measured after 5 min exposure to 10200 lx of D65 light.



Note 1: Doping with two rare earth ion activators provides the longest duration afterglow.

Note 2: Afterglow duration greatly exceeds earlier generation of doped zinc sulfides.

Note 3: Phosphorescence decay time is defined as elapsed time from the moment stimulating irradiation is terminated until the intensity of light emission is reduced to the threshold value 0.32 mcd/m² (100 times the perception limit of the human eye.)

devices are now limited to the use of tritium due to its low radiological toxicity and commercial availability and the fact that luminescence duration is continuous without the need for a “charging” light source. Despite the relative limitation in afterglow intensity and duration of light charged ZnS phosphors, the market and potential applications for persistent luminescent products continued to grow.

Rare earth activated phosphors; a persistent phosphorescent game changer

In 1996, Matsuzawa et al. published an article revealing an entirely new approach to the field of persistent phosphorescence by demonstrating that an alkaline earth aluminate, an inorganic crystalline material codoped

with the rare earths Europium (Eu) and Dysprosium (Dy), when charged by exposure to natural daylight (which contains a UV component) produced a persistent initial afterglow of higher intensity and far longer duration than corresponding ZnS doped phosphors. For many applications, the newer generation strontium aluminate phosphors, especially the example of doping with Europium/Dysprosium (SrAl₂O₄:Eu²⁺,Dy³⁺) is an order of magnitude (≈ 10 X) afterglow duration and intensity of the preceding generation of phosphors as exemplified by doped ZnS.

Matsuzawa’s results stimulated a resurgence in the search for persistent phosphors activated by rare earths and eventually yielded a new range of persistent phosphors comprised primarily of rare earth activated alkaline earth

Table 1. Comparison of afterglow intensity and duration of doped Zinc Sulfide and doped Strontium Aluminate phosphors after charging^{1,2}

Afterglow luminance mcd/m ²	<u>ZnS:Cu,Co</u>		<u>SrAl₂O₄:Eu²⁺,Dy³⁺</u>		<u>Time after charging</u>
	A	B	A	B	
	30	38	380	380	10 min.
	3	3	130	120	30 min.
	0	0	48	45	60 min

Trial A. Light source intensity and charging time unreported

Trial B. 10 min exposure to 200 lx of D₆₅ light

Note 1: Afterglow intensity and duration may be limited under very short charging time and/or insufficiently energetic illumination.

Note 2: Afterglow intensity and duration values are for pure phosphor and may vary in product applications although is not likely to affect the relative superiority of Strontium Aluminate to Zinc Sulfide in phosphorescent afterglow intensity and duration.

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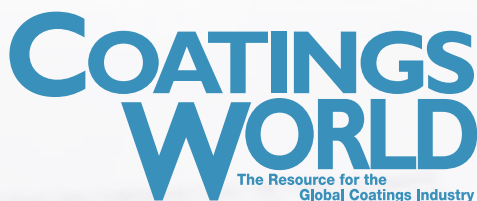


Figure 3. Rare earth activated strontium aluminate afterglow configured for different principal emission wavelengths.

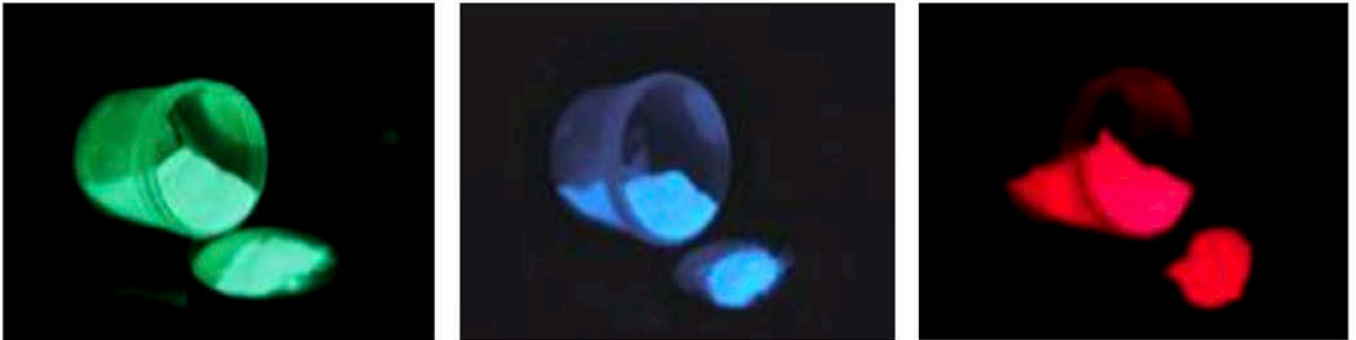


Figure 4. Typical examples of persistent-phosphor incorporation in self-luminous way-finding and emergency signage, novelty self-luminous printing and self-luminous polymer film.



aluminates, silicates and aluminosilicates with afterglow intensities and durations far exceeding that of the previous generation of activated zinc sulfide phosphors. These enhanced luminance characteristics enabled formulation of a host of visual products extending the capabilities of the earlier generation of phosphors.

The new generation of persistent phosphorescent materials with their extended afterglow duration and intensity made possible enhanced performance in safety and directional indications created with self-luminous paints and polymer-encapsulated pigments as well as both generic and custom preformed devices employed for emergency signage, traffic direction and way finding systems. Subdivided to enable dispersion in appropriate vehicles has also made

possible the development of self-luminous inks for printing on textile, packaging and other surfaces and for use in anticounterfeiting, information encryption/authentication and security applications all with greater afterglow intensity and duration than previously possible in light charging systems. Like other plastic pigments, these phosphors can be incorporated in a range of polymer resins to produce phosphorescent sheet and formed objects. A broad range of applications in biomedical imaging and dosimetry are also suggested and are being investigated.

Phosphor crystalline structure affects emission wavelength

Rare earth activated phosphors, such as the europium

Figure 5. Crystal of generic Eu doped strontium aluminate.

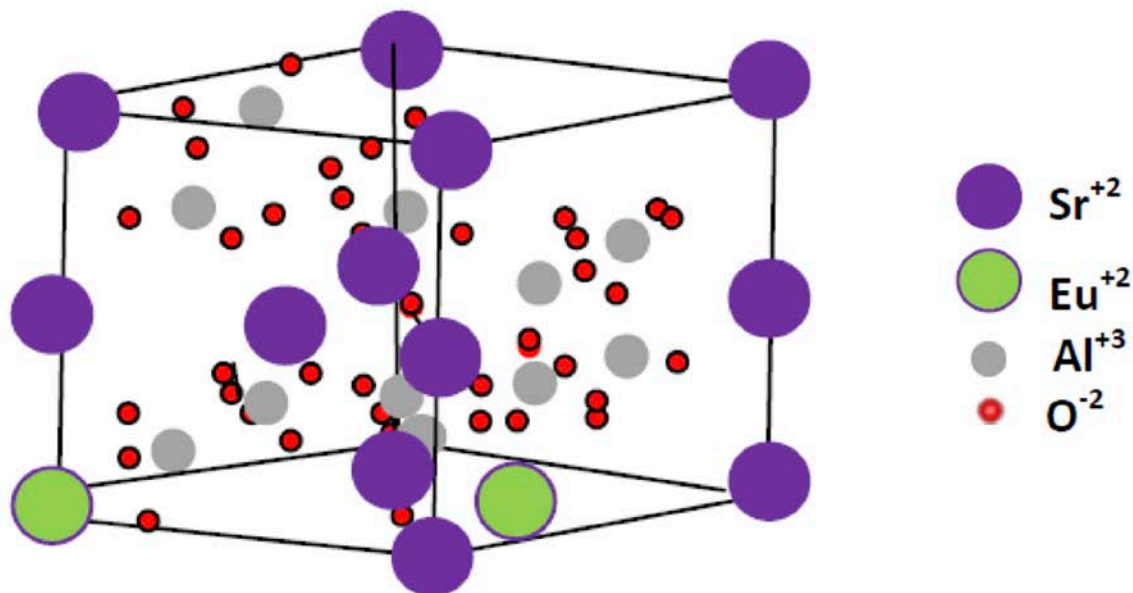


Figure 6.

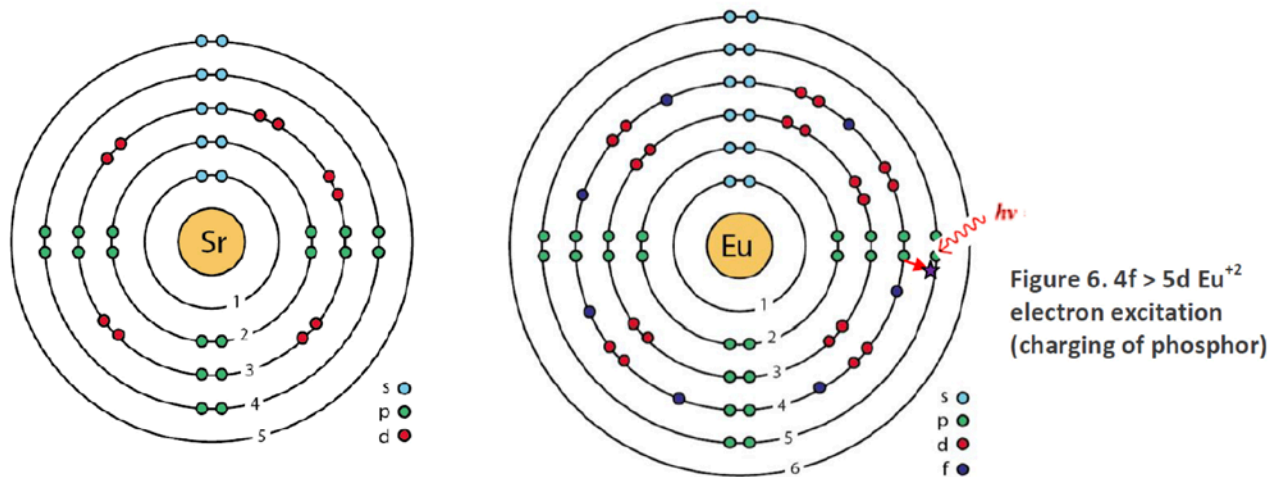


Figure 6. 4f > 5d Eu⁺² electron excitation (charging of phosphor)

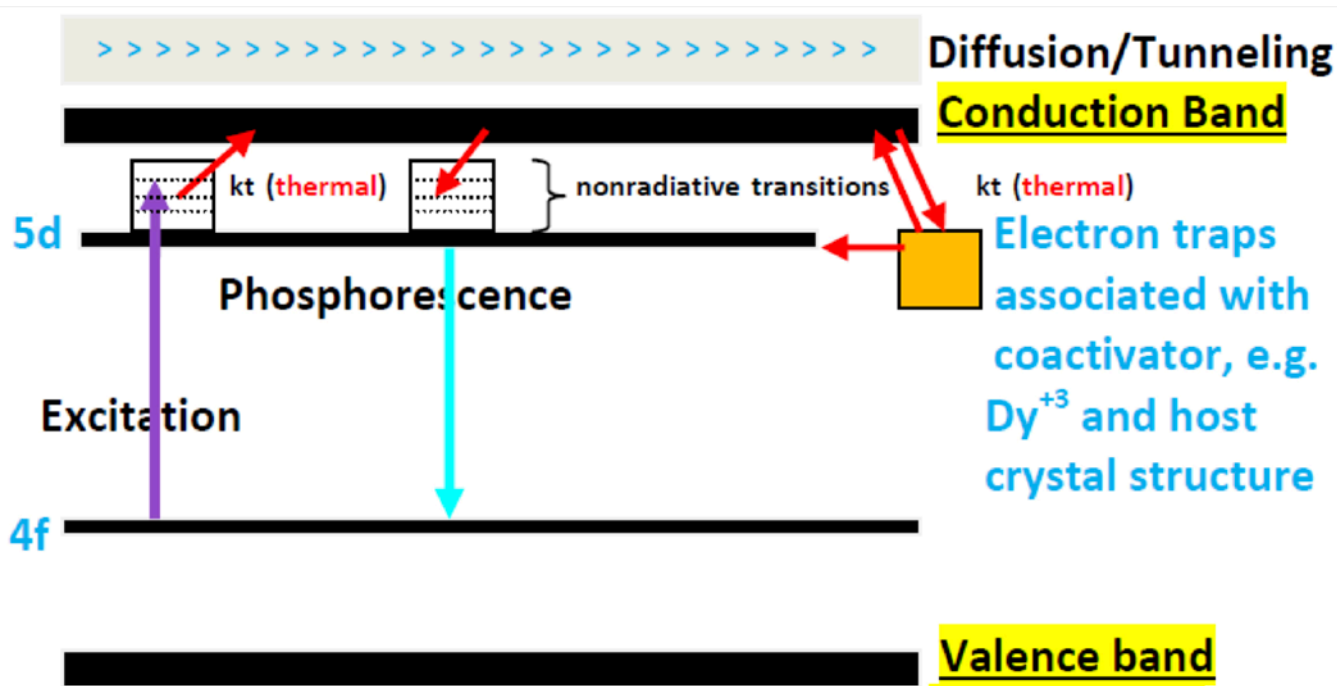
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activated strontium aluminates, represent more than a singular group of substances despite the fact they are composed of the same elements; strontium, aluminum and oxygen. This is because there are a variety of ways that the elements comprising the phosphor can associate in number and arrangement. Each of these arrangements will have characteristic energies which in turn will affect the primary frequencies of light associated with its phosphorescence. This means that control of the relative number of each of the atoms forming the phosphor as well as the crystal form in which those atoms are arranged can result in phosphor species with different afterglow wavelengths. Developing synthesis methods capable of

generating phosphor species with the desired afterglow wavelength, intensity and duration is the domain of the chemist and noting how many different approaches are described in the scientific literature is no doubt a painstaking task.

Europium and Dysprosium are not the only effective rare earth activating substances. In fact, there is a whole of range of such activators which can influence the wavelength of the phosphorescent afterglow by controlling the associated energy of the electronic transitions that are its source. To make matters even more complex, ratios of the base phosphor and the activator can produce a further extension of afterglow wavelengths and intensities.

Figure 7. Simplified illustration of the mechanism for persistent phosphorescence.



The host, typically a crystalline material such as an alkaline earth aluminate, is doped with a small percentage of a rare earth activator which introduces available electron energy levels in the vicinity of the host conduction band's energy level. Exposure to appropriate wavelength(s) of radiant energy excites lower level activator electrons to fill higher energy vacant orbitals which may act as traps. Ambient thermal energy raises the trapped electrons to the conduction band from which they return to their initial state emitting radiant energy seen as light of a wavelength corresponding to the energy difference between the lower and upper orbital energy; i.e., the phosphorescent afterglow. In addition, the host crystal itself (as well as secondary dopants) may provide additional trapping levels that bind excited electrons which are thermally promoted over time back to the conduction band from which phosphorescent emission takes place. Duration of phosphorescence is a function of the number of filled traps and the efficiency of thermal interactions generating phosphorescence.

Note: The foregoing description is a generalization of a range of different approaches to modeling persistent phosphorescent processes that are well beyond the technical level of the discussion presented here.

Structure and mechanism overview of persistent phosphorescence afterglow

Aluminates, aluminosilicates, and silicates are minerals; regular arrangements of atoms in a repeating pattern termed a crystal lattice. This pattern can actually be viewed with an electron microscope or discerned by techniques such as X-ray diffraction which is able to resolve the orderly atomic arrangement of substances in geometric crystal lattices. Figure 5 gives an example of a generic strontium aluminate unit crystal in which a small percentage of the Sr⁺² ions are substituted with europium ions (Eu⁺²).

The links that hold these atoms together in various configurations are the result of sharing electrons. This is the definition of a chemical bond and it occurs because bond formation is energetically favored. When the electrons of

combining atoms are shared unequally the bonding is termed ionic and occurs between negatively and positively charged atoms. The ability of participant atoms to bond to multiple partners, as in the persistent phosphors, results in the geometric arrangement of ions termed a crystal lattice. This is the case with the generic strontium aluminate depicted above in which a small fraction of the Sr⁺² ions are substituted by Eu⁺². This substitution is enabled because both Sr⁺² and Eu⁺², 1.21 and 1.20 Å, respectively, are approximately the same size and comparable relationships hold for other phosphorescent enabling ions integrated into host crystal lattice defects.

Understanding how light can charge a phosphor and how that light energy is released over time and at different wavelengths can best be explained in terms of the atomic

Figure 8. Combined daylight fluorescent/persistent phosphorescent colorant

Dual Colorant



arrangement and energizing of electrons within the doped host crystal. This, in turn, requires some basic definitions. Figure 6 is a very basic comparative model of the Strontium and Europium atoms' electronic arrangement. At the center of each atom is the positively charged nucleus (not shown) surrounded by a series of shells containing negatively charged electrons at different energy levels dependent on the distance of these shells from the nucleus. The outermost occupied shell is termed the valence band and these are the electrons that form molecules by sharing with electrons from other atoms and propagate as the crystal frameworks depicted in Figure 5.

Examination of the models show that both Sr and Eu have outermost shells or valence bands with two electrons and that is why in combining with other atoms by donating or sharing these electrons they form doubly charged positive ions, Sr^{+2} and Eu^{+2} . Further inspection indicates that Eu has more electron shells and more electrons than Sr. It is this distinction that enables Eu to foster persistent phosphorescent characteristics when incorporated in aluminates and other minerals that provide a crystalline substrate for this process.

Electrons within the atom maintain a specific energy in relation to the nucleus and this does not change save for specific interactions with appropriate sources of energy. These interactions are usually with the electromagnetic spectrum (although there are other possibilities), which comprise a continuum expressed in terms of frequencies or wavelengths from the ultraviolet and above to the visible to the infrared

and below. This interaction is “quantized,” a difficult concept to communicate, but radiatively energized electron transitions to higher energy levels take place only when the energy absorbed equals the energy difference between those levels. Similarly, loss of energy by excited electrons may be accompanied by the emission of radiation of a specific wavelength, also quantized. This is, for example, how astronomers are able to determine the elemental composition of stars by measuring the wavelengths of the light emitted which are characteristic of the energy level transitions of their constituent atomic electrons.

The simplified atomic structures depicted in Figure 6 have further important complexities (not shown) involved in generating persistent phosphorescence, namely, the specific Eu^{+2} electron transitions which participate in the process. Referring to Figure 6, it is the outermost or valence electrons, 4s in Strontium and 5s in Europium which participate in the bonding that forms the lattice of the host crystal. In the case of Eu^{+2} , it is believed that a transition of a lower level 4f electron to a 5d level is facilitated by exposure to energy of a wavelength in the UV separately or as a component of sunlight equal to or greater than the difference between these two electronic energy levels and that once this transition takes place the electron is “trapped” until a subsequent process liberates it. This energy, released over a duration of time as visible light, is termed the persistent phosphorescence afterglow.

Figure 7 diagrams the persistent phosphorescent process

from the trap state of the energized electron via the conduction band of the atom. The conduction band is the electron level above the valence band where electrons can flow freely. The smaller the energy level difference between the valence band, where electrons are tightly confined, the more metallic the nature of the atom involved and the more easily valence and inner electrons can reach this level. Copper (Cu), for example, has a relatively small energy difference between its valence and conduction band which makes it an ideal conductor for electrons as in the doping of ZnS or as a source of the current in common electrical wiring. Semiconductors, by contrast, are nonmetals doped with materials capable of generating free positive or negative charges which can then be controlled in various types of circuits.

In the case of Eu^{+2} activated phosphors, it is believed that the energy difference between the excited electron in the 5d orbital and the conduction band is sufficiently small that thermal energy, i.e., ambient temperature (heat) of the environment is sufficient to excite the Eu^{+2} trapped 5d orbital electron into the atom's conduction band from which transition back to its original state occurs with the release of visible light of a wavelength corresponding to that energy difference. In some cases, a second rare earth ion (not shown) such as Dysprosium (Dy^{+3}), is incorporated along with Eu^{+2} creating more electron traps and therefore greater intensity and duration in phosphorescent persistence. **CW**

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