

Persistent Luminescence Beats the Afterglow: 400 Years of Persistent Luminescence

by **Jorma Hölsä**

Persistent luminescence is a phenomenon where the material is emitting—usually in the visible range—for hours after the irradiation (or excitation) source has been switched off.¹ The irradiation used may be visible light or UV, X-ray, or gamma radiation. Persistent luminescence has been, and still is, unfortunately in a misleading manner, called phosphorescence because of the long emission time. Phosphorescence may be an appropriate term to be used in the context of luminescence from organic compounds involving triplet-to-singlet transitions. These are forbidden with a long decay time but are otherwise perfectly natural. The long decay time of persistent luminescence, however, is due to the storage of the excitation energy by traps and is released from them with thermal energy. Thus the term thermally stimulated luminescence (TSL) is appropriate but for the sake of brevity, the phenomenon is called, in what follows, persistent luminescence.

The Glorious Past

The well-documented history of persistent luminescence as a phenomenon dates from the beginning of the 17th century.² In 1602, an Italian shoemaker, V. Casciarolo, observed strong luminescence from a mineral barite, BaSO₄, later to be known as the famous Bologna stone. It appears, however, that the material actually was not the barite mineral itself but rather the reduced product, barium sulfide, BaS. According to modern knowledge, the reduction process of the sulfide cannot be held responsible for the luminescence since this luminescence occurred long after the process had been terminated. On the other hand, taking into account the low purity of both the original barite and the charcoal used for the reduction, it is evident that a lot of different (trace) impurities were present. That is probably the reason for the varying color of the persistent emission reported, though mainly orange or red emission in the visible range prevails in the literature. Whatever the emission remained unknown then and, to certain extent, up to the 21st century. At that time, *i.e.*, during the decades following the discovery of the bright emission from the (reduced) Bologna stone, the phenomenon did not cease to arouse the interest of both scientists and laymen, and even several books were written on this miraculous phenomenon (see Fig. 1).

The matter clearly went beyond the knowledge of the scientists of the time, and, maybe for comprehensible reasons, even the famous interdisciplinary genius Galileo refused to get involved. Probably Galileo had had enough trouble with the Catholic Church and he preferred to leave the shine of the Bologna stone alone since it may have been of celestial origin. Since the 17th century, only scattered reports are available on persistent luminescence and the research receded considerably because no explanation was found for the persistent luminescence produced without any evident excitation source.

From the above, it may well be concluded that persistent luminescence was one of the first genres of luminescence ever discovered and studied to some scientific extent. Despite no explanation being found for the persistent luminescence, the applications were taken into use in the 20th century. Luminous paints were based on persistent luminescence from the different sulfide materials as ZnS doped with *e.g.*, Cu.¹ The emission was modified with the partial substitution of Zn with Cd. However, at its best, persistent luminescence from these materials was both weak and short, lasting for a few hours only. Some environmentally dubious “tricks,” such as the doping of ZnS with radioactive elements (one of the few uses of the

artificial radioactive lanthanide, promethium), were used in order to prolong the duration of persistence with external excitation. These tricks were only retarding the final rejection of the ZnS based phosphors, also due to their pronounced instability against humidity.

The leading role of persistent luminescence as the number one luminescence subject was finally lost with the advent of the introduction of the rare earth based phosphors in the 1960s. This state of affairs seemed to remain even while the other fields of luminescence flourished, for example in the areas of lighting, cathode ray tubes, and scintillator material applications. The hectic research and development which followed the lanthanides now being commercially available in a pure form (incidentally as a byproduct of the Manhattan project!) produced both new information about the different luminescence processes and ever better phosphor materials. None of this took place in the persistent luminescence field. As a result of the speeded-up introduction of many new phosphor materials, also some with serious problems with the resistance to the some times hostile operating conditions (*e.g.* mercury vapor and electron bombardment) appeared in the commercial market. Thus the negative side of persistent luminescence

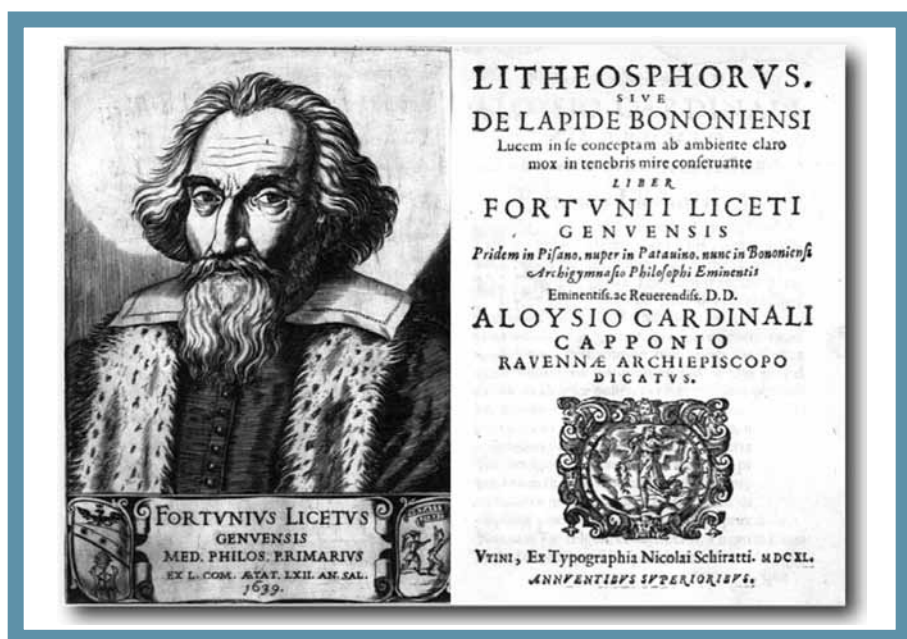


Fig. 1. The book *Litheosporus Sive de Lapide Bononiensi* by Fortunius Licetus (Bologna, Italy, 1640) on the persistent luminescence of the Bologna stone.

was introduced: the afterglow. As a result of the formation of traps³ to store the excitation energy (e.g., UV radiation, electrons) the emission was retarded³ and, in many cases, also significantly weakened.⁴ This was not always completely condemning the phosphor material since different ways to solve these problems were finally developed, e.g., post-treatment in inert/reactive atmosphere or introduction of some additives.^{4,5} However, in general, the afterglow problem seemed to give persistent luminescence the final *coup de grâce* and practically nothing, neither in understanding the phenomenon nor in developing new materials, took place before the mid 1990s.

The New Persistent Luminescence Era

Then, out of the blue, the first generation of the modern persistent luminescence materials, the Eu²⁺ doped and rare earth (R³⁺) co-doped alkaline earth aluminates (MAl₂O₄:Eu²⁺,R³⁺; M: Ca and Sr) appeared in both the commercial market and in research laboratories as well.⁶ With this, the first new persistent luminescence era since 1995, there rapidly appeared not only new materials and mechanisms but also new methods of analysis and applications. As a result of the increased research activity, there emerged also hundreds of papers, reports, and meeting communications.



FIG. 2. The persistent luminescence behavior of the blue emitting Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ (E), green emitting SrAl₂O₄:Eu²⁺,Dy³⁺ (C) and red emitting Y₂O₂S:Eu³⁺,Mg²⁺,Ti^{IV} (S) phosphors in day light, under UV excitation, and in dark.

Unfortunately, since the persistent luminescence phenomenon seemed to be rather complicated, the quality of the reports has not always been of the best caliber.

As the new persistent luminescence materials have been developed, there are presently persistent luminescence phosphors for each of the main colors: blue, green, and red that fulfill—perhaps with the exception of red—the requirements for not only sufficiently strong and long persistent luminescence but also for the stability of a commercial phosphor. Figure 2 shows the behavior of three different persistent luminescence phosphors in daylight, under UV radiation excitation, and in dark after UV irradiation. Despite the high initial persistent luminescence of the red emitting material, Y₂O₂S:Eu³⁺,Mg²⁺,Ti^{IV}, its long term luminescence is much weaker than the duration of the blue (Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺; 25+ hours) and green (SrAl₂O₄:Eu²⁺,Dy³⁺; 15+ hours) emitting counterparts.

The idea of mutating a well-established and commercially available phosphor for other luminescence applications such as Y₂O₂S:Eu³⁺—though reinforced with co-dopants such as Mg²⁺ and Ti^{IV}—does not always result in a superior persistent luminescence material, as was the case with SrAl₂O₄:Eu²⁺. The design of new efficient persistent luminescence phosphors requires more than this; or a lot of luck. As a result of perhaps the latter, the most recent persistent luminescence phosphors, the Eu²⁺ doped and rare earth (R³⁺) co-doped alkaline earth disilicates⁷ (M₂MgSi₂O₇:Eu²⁺,R³⁺; M: Ca and Sr) were discovered to be much more efficient and stable than corresponding

aluminates. Their manufacture is also somewhat less complicated, as no flux material is needed. The host materials (both MAl₂O₄ and M₂MgSi₂O₇, but not Y₂O₂S) are basically rather cheap, though the high purity requirements increase the price tag. So far there has not been any serious alternative for the emitting Eu²⁺ dopant (the price of which is sky-rocketing), mainly because of the very favorable position of its ground electronic energy level *vis-à-vis* the host band structure.⁸ The low concentration of this element somewhat lowers the price, which is inherently high because europium is used in most luminescence applications, including as security markers in Euro bank notes.

The idea of making a white emitting persistent light source by combining the three individual blue, green, and red emitting phosphors, in a way similar to the tricolor fluorescent tubes, seems possible when the emission spectra of these phosphors are considered alone (see Fig. 3). However, the unbalanced duration of the three colors, especially due to the weak and short red persistent emission, will delay or even preclude this application. Instead, there are many more or less well established ones, such as sensor applications including temperature sensing but also changes in pressure (on airplane wings, for example). The use of nanoparticulate persistent luminescence materials for biomedical applications with direct *in situ* imaging sounds both interesting and feasible. However, it is quite certain that the commonplace, less exciting applications using persistent luminous paints will dominate the market for at least the near future.

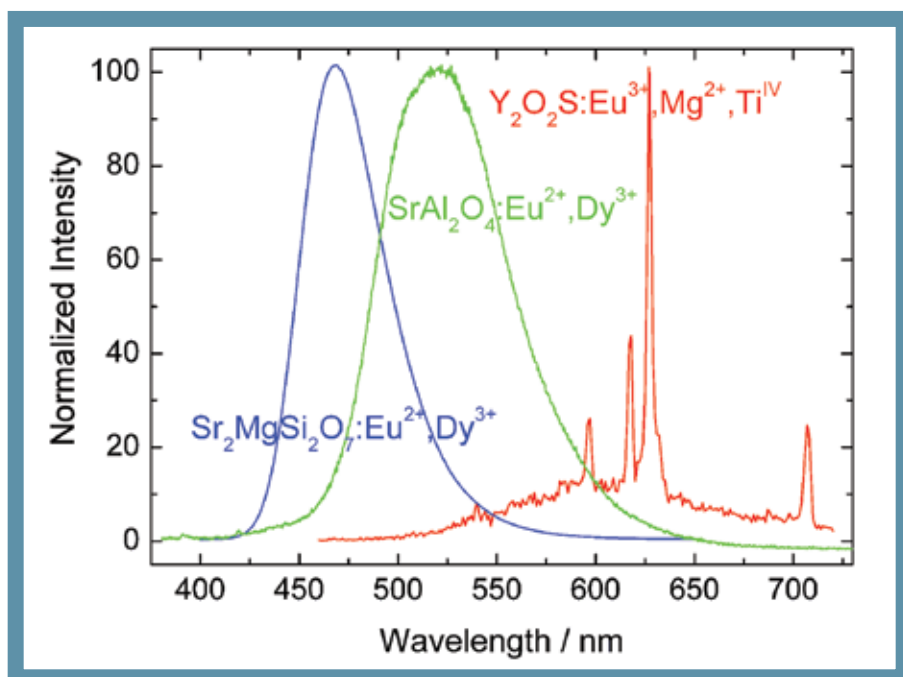


FIG. 3. The luminescence spectra of the blue emitting Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺, green emitting SrAl₂O₄:Eu²⁺,Dy³⁺, and red emitting Y₂O₂S:Eu³⁺,Mg²⁺,Ti^{IV} phosphors after UV excitation.

The Mechanism

The design of new persistent luminescence materials would probably be much facilitated if the mechanism(s) of the phenomenon were known. The research of persistent luminescence has thus been focused on two intertwined objectives: the development of new materials, especially the red emitting ones, and the mechanism(s) of persistent luminescence. The latter studies have produced more papers than good ideas in the past. In most cases, one of the two most important factors have been ignored: the energetics deciding the nature of charge carriers or the nature and energetic positions of the defects where the excitation energy is stored for further use as persistent luminescence. Since 2005, persistent luminescence mechanisms have somewhat converged into what is known now, though there is not really any widespread agreement on the details. In Fig. 4 these factors are presented in a schematic and simplified way for one of the best persistent luminescence phosphors, $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{R}^{3+}$, modified from that of $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$.⁹

The irradiation of the material by blue light (or UV radiation) results in the photoexcitation of Eu^{2+} via the $4f^7 \rightarrow 4f^65d^1$ transitions which, as stated above, overlap with the conduction band of $\text{Sr}_2\text{MgSi}_2\text{O}_7$. The capture of the excited electron by the conduction band may take place directly or may be assisted by thermal energy since the life time of the conventional Eu^{2+} luminescence in aluminates is rather long, about 1 μs .¹⁰ The electron can move in the conduction band until it returns to the europium center or is captured by the traps close to the bottom of the conduction band. The actual persistent luminescence involves the temperature controlled gradual release of the trapped electrons followed by the migration of electrons to the europium center through the conduction band. The recombination produces the persistent emission. No evident pitfalls exist in this mechanism though proving that is hard due to the ubiquitous uncertainty about the thermally controlled mechanism. Despite the apparent incompatibility in energies between the thermal energy at room temperature (ca. 25 meV) stimulating the persistent luminescence and those used in synchrotron radiation methods (UV-VUV: 5 eV; XANES and EXAFS: 5-20 keV), these methods have been found very useful in the study of persistent luminescence mechanisms.^{11,12}

The challenge to find an efficient red emitting persistent luminescence material has been found quite hard since the best candidate as the emitting

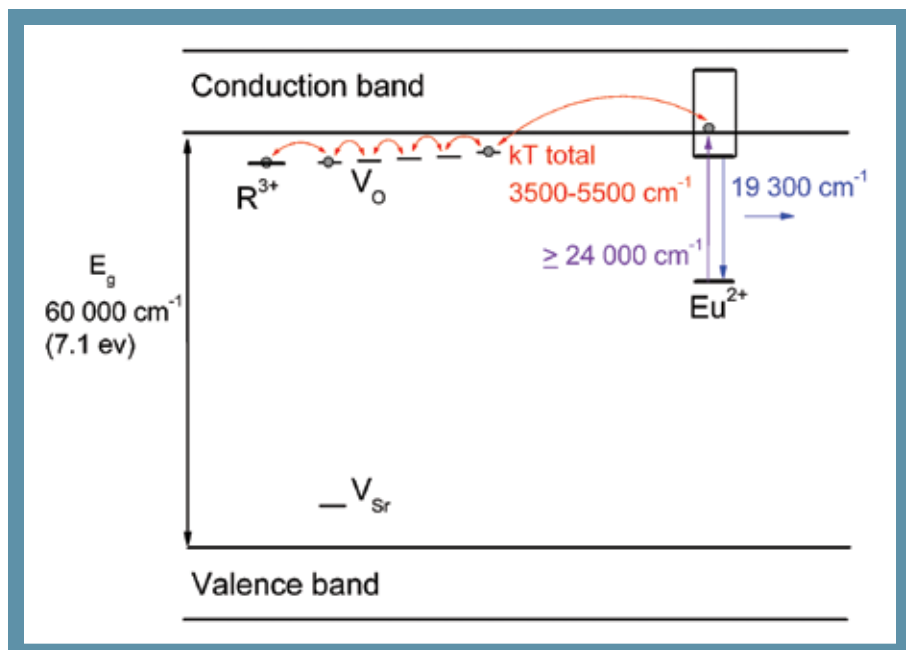


Fig. 4. The persistent luminescence mechanism of the blue emitting $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{R}^{3+}$ phosphors.

center in persistent luminescence materials is the Eu^{2+} ion. The strength of the crystal field effect (*i.e.*, the predominantly electrostatic effect of neighboring ions onto Eu^{2+}) required to lower the lowest emitting level of the $4f^65d^1$ electron configuration to energies low enough to produce red emission is very high (Fig. 5).

Among the few potential candidates, the $\text{Ca}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+},\text{R}^{3+}$ materials¹³ seem

to be the most promising ones. If the use of Eu^{2+} as the emitting center is discarded, the Mn^{2+} red emission, despite the very difficult excitation, can be used. The challenge of weak excitation can be circumvented by the use of the Eu^{2+} ion as the absorbing and energy storage species. Persistent emission can be obtained with the aid of Eu^{2+} to Mn^{2+} energy transfer.¹⁴

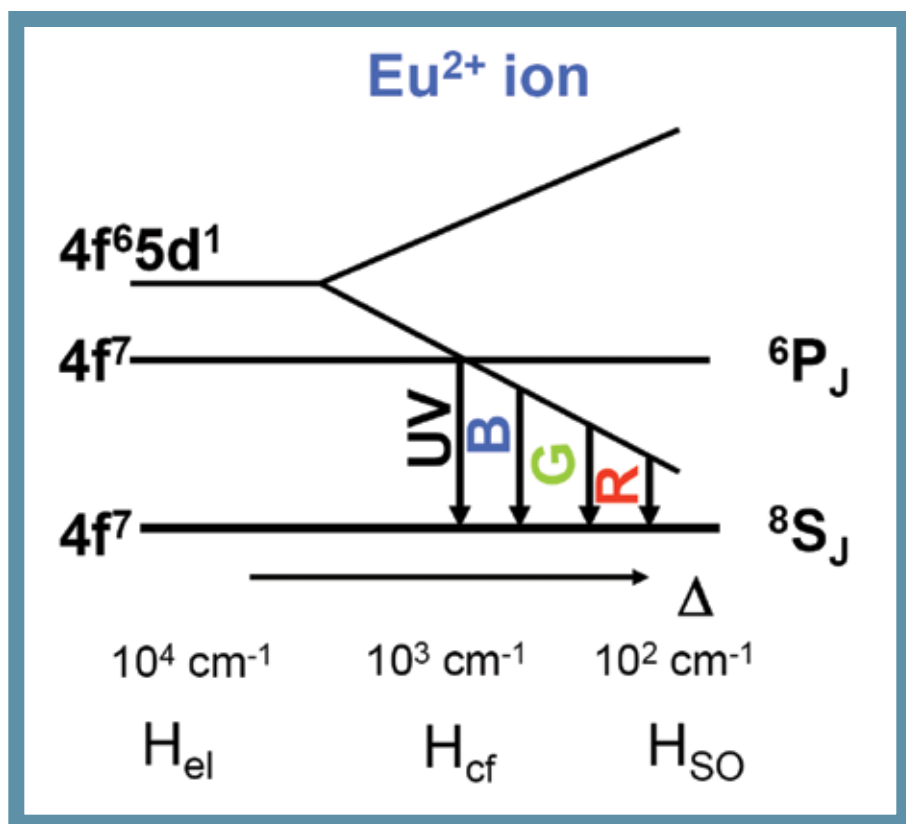


Fig. 5. The effect of crystal field strength on the energy levels and emission color of the Eu^{2+} ion in solid state.

Conclusion and Future

Persistent luminescence phosphors are here to stay and their applications are rapidly expanding from bulk materials visible to everyone (e.g., exit signalization on airplane cabin floors) to high tech products (e.g., biomedical imaging). The elaboration of persistent luminescence mechanisms is advancing at a rapid pace and these have been basically solved, though the refinement of the details is still needed. On the application side, the challenge of finding an efficient red emitting persistent phosphor is still waiting. Finally, the rapid development of theoretical methods, mainly based on density functional theory (DFT) and increased computational capabilities, have given promising results in the calculation of practically all those issues of persistent luminescence now determined experimentally. The hangover caused by the afterglow shown by many a commercial phosphor is now overcome. As a result, persistent luminescence has resumed its place in the front line in the research of luminescence phenomena. At the same time, persistent luminescence research has offered the means (e.g., thermoluminescence) and knowledge (e.g., defect chemistry and physics) to solve the afterglow problems.

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