

LUMINESCENT MATERIALS AND APPLICATIONS

M. NAZAROV

Institute of Applied Physics
Academy Sciences of Moldova
Republic of Moldova
e-mail: mvnazarov@mail.ru

Abstract

Short review of the past and present of luminescent materials is given to show a major phosphor's applications in traditional display, flat panel display, lighting, medical, security etc. Multiphase micro and nanoparticle persistent phosphors are synthesized and applied for different fields including painting, medical and biological investigations. A lot of examples show a broad range of applications of persistent luminescence from bulk materials to high tech products, especially in medicine. The development of high efficiency nanosized phosphor makes it possible to propose persistent materials as very good candidates for photodynamic therapy of cancer. An artificial block from slag, concrete, and sand covered with $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} based phosphor is prepared, and a new direction in biology for algae cultivation and artificial reef is discussed. For the first time, underwater luminescence is experimentally studied under real sea conditions. Bright blue-green long-lasting afterglow is registered at a depth of 5m.

Keywords and phrases: luminescent materials, persistent luminescence, underwater luminescence.

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1. Introduction

A phosphor is a material that emits light as a result of absorbing energy (Figure 1). Luminescence is the term given to the emission of this light.

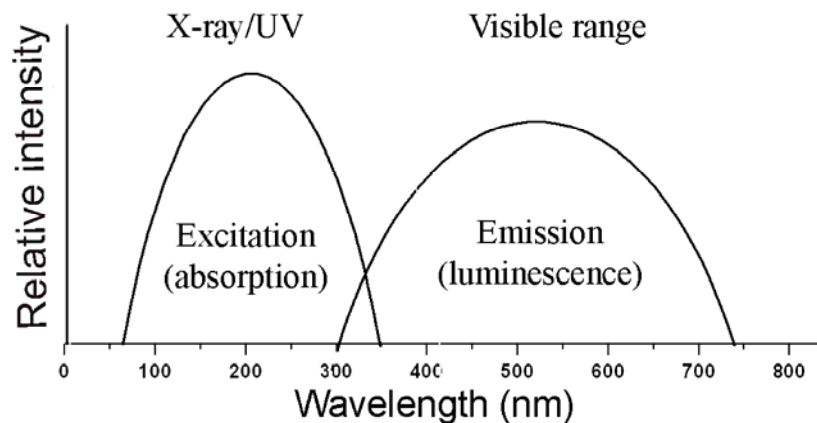


Figure 1. Diagram illustrating the energy absorbed by a phosphor (left), which is then transformed to emitted light of lower energy (right).

Hundreds of thousands of phosphors have been synthesized, each one having its own characteristic colour of emission and period of time during which light is emitted after excitation ceases. Most phosphors are composed of a transparent microcrystalline host (or a matrix) and an activator, i.e., a small amount of intentionally added impurity atoms distributed in the host crystal.

Inorganic luminescent materials have been known since approximately the tenth century in China and Japan as well as since the end of the middle ages in Europe. The detailed history of luminescence can be found in one of the early book of Harvey [1] or in a special review dedicated to the 100 years of research and application of inorganic luminescent materials [2].

2. The Past and Present of Phosphors

It is said that an alchemist, Vincentinus Casciarolo of Bologna, Italy, found a heavy crystalline stone with a gloss at the foot of a volcano, and fired it in a charcoal oven intending to convert it to a noble metal. He obtained no metals but found that the sintered stone emitted red light in the dark after exposure to sunlight. This stone was called the “Bolognian stone” [3]. From the knowledge now known, the stone found appears to have been barite (BaSO_4), with the fired product being BaS, which is now known to be a host for phosphor materials.

At the end of the nineteenth century, a first major milestone concerning luminescent materials and devices was the realization of gas discharges and electron beams in evacuated glass tubes by Geissler and Braun, as well as the discovery of X-rays by Roentgen. The visualization of gas discharges, cathode rays, or X-rays represent also the first practical uses of luminescent materials. Based on these fundamental results, the first luminescent devices were developed only a few years later, and included cathode-ray tubes, fluorescent lamps, and X-ray intensifying screens. Thereafter, research on cathode-ray tubes and the relevant phosphors was stimulated during the Second World War for use in radar screens. In addition, the rapid and successful application of fluorescent lamps for illumination purposes, as well as the use of X-rays for medical imaging, intensified research on novel luminescent materials in the first half of the twentieth century. The first luminescent devices contained only a single phosphor material. The emitted light was normally not white, but coloured. For instance, blue-emitting CaWO_4 , which is a highly efficient phosphor, was used in X-ray-intensifying screens in Braun’s early cathode-ray tubes as well as in the first fluorescent lamps by Edison. Lighting became more colourful with so-called zeon or neon tubes. Based on neon, argon, or mercury discharges in combination with different phosphors and coloured glass, different coloured lamps were realized. These lamps were presented by Claude at the world exhibition in 1937 in Paris and used for advertising [4]. For illumination purposes, however, the emission of white light is required.

Some single-phosphor lamps were proposed, but their emission was too low. Nowadays, tri-colour phosphor mixtures are used in fluorescent lamps worldwide. Fluorescent tubes and compact fluorescent lamps became widely available in the 1950s and early 1990s, respectively. Along with high-intensity discharge lamps, they offer a longer life and lower power consumption than incandescent sources, and have become the mainstream lighting technology in homes, offices, and public places.

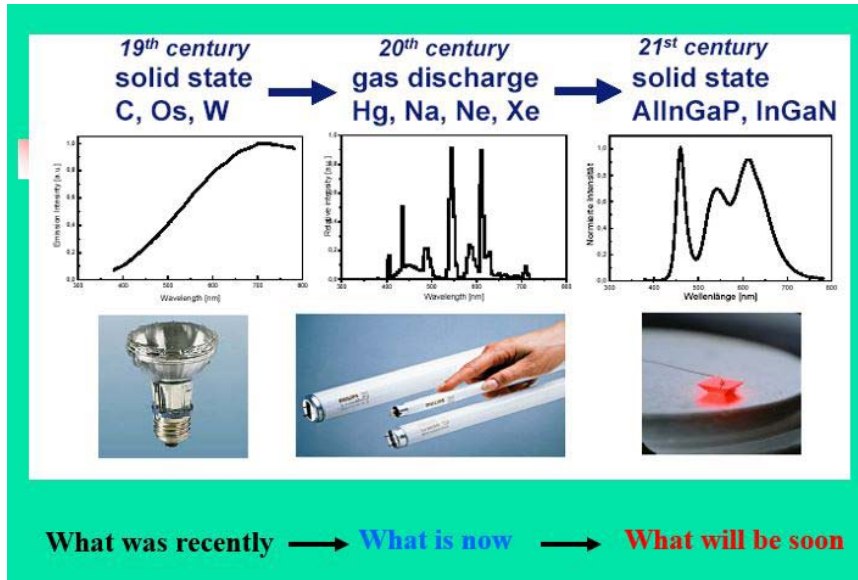


Figure 2. From incandescent sources to solid-state light sources.

More than a century after the introduction of incandescent lighting and half a century after the introduction of fluorescent lighting, solid-state light sources are revolutionizing an increasing number of applications. Whereas the efficiency of conventional incandescent and fluorescent lights is limited by fundamental factors that cannot be overcome, the efficiency of solid-state sources is limited only by human creativity and imagination. The high efficiency of solid-state sources already provides energy savings and environmental benefits in a number of applications. For example, conventional incandescent or fluorescent lamps rely on either incandescence or discharge in gases. Both

phenomena are associated with large energy losses that occur because of the high temperatures and large Stokes shifts involved. Light-emitting diodes using semiconductors offer an alternative method of illumination. The operation of LEDs is based on spontaneous light emission in semiconductors, which is due to the radiative recombination of excess electrons and holes that are produced by the injection of current with small energy losses. Subsequently, the radiative recombination of the injected carriers may attain quantum yields close to unity. As a result, compared with conventional lamps, LED-based light sources have superior lifetime, efficiency, and reliability, which promise significant reductions in power consumption and pollution from fossil fuel power plants. Currently, LEDs are widely used as indicators, rear lamps for vehicles, decorated lamps, backlights for cellular phones and liquid crystal displays, and small-area lighting. With advances in the brightness and colour-rendering properties of LEDs, it is generally accepted that they will replace conventional lamps for general lighting in the near future.

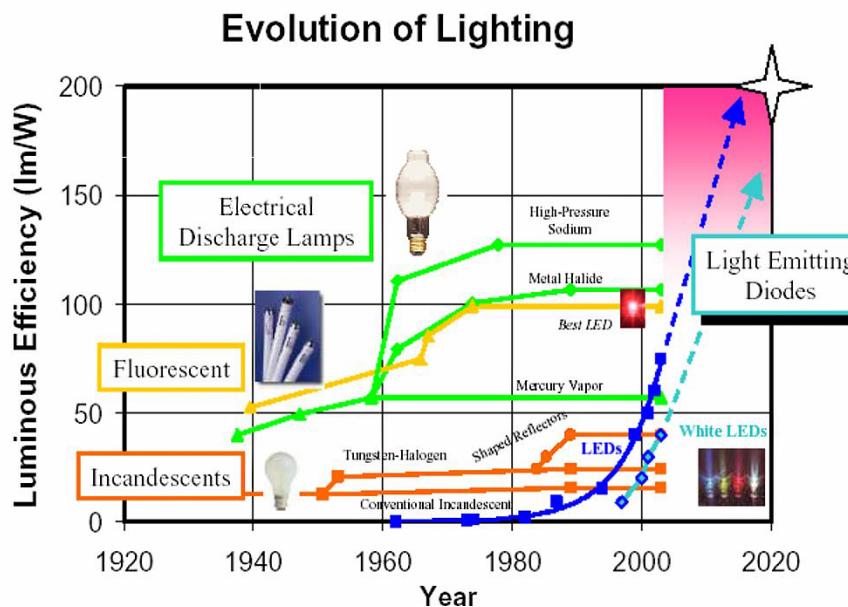


Figure 3. Evolution of lighting.

Hundreds of phosphors are available for excitation at 250nm, the dominant emission band of Hg lamps. In solid-state lighting, however, the excitation wavelength is much longer, typically in the range 380 to 480nm. New high-efficiency phosphors, which can be efficiently excited at these wavelengths, are now being developed. Whereas high efficiency yellow phosphors are readily available (e.g., cesium-doped yttrium aluminum garnet- $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) phosphors), the efficiency of red phosphors still lags. As a novel class of inorganic phosphors, oxynitride and nitride luminescent materials have received considerable attention because of their potential applications in solid-state lightings and displays. Some of them are discussed in this review.

Why the luminescent materials?

(1) High lumen output

LED has eight time more brightness than incandescent lamps without emissions harmful to the environment.

(2) Tremendous energy savings

High power LED light sources are extremely efficient returning a 50 to 80% saving over conventional sodium or mercury lamps.

(3) Long life

Operating for an average of 10 hours per day LED has a life span of up to 13 years, 50,000 hours. Unlike traditional light bulbs, LED is not fragile and susceptible to breakage or vandalism.

(4) High colour index

LED has an unique colour index providing bright, true colours during night-time hours.

(5) No dust absorption or yellowing

Because LED operates at low voltage and low temperature there is no reduction in brightness or yellowing, which is associated with traditional street lighting, over the life span of the LED.

(6) Instant start

Unlike sodium lights, LED lights do not require a time delay to reach optimum brightness levels.

3. Major Phosphor's Applications

Luminescent materials are well known for a long time from traditional lighting and display applications, like cathode-ray (television) tubes, fluorescent lamps but also X-ray screens. Exploration of novel materials classes during the last years has enabled development of new applications, e.g., white LEDs, plasma display panels, bio-markers, and solar cells. Recent progress and future prospects show that luminescent materials remain not only interesting from a scientific point of view but also relevant from an application point of view. For many years to come, scientific challenges as well as societal needs in this research field can be addressed by chemists, physicists, and materials scientists. This presentation reviews the latest developments on these novel luminescent materials, their preparation, crystal chemistry, characterization, and optical properties. The intention is to focus on the relationship between the luminescence properties on the one hand and the chemical composition and structure on the other.

The research on luminescent materials is stimulated by various applications. Luminescent materials are widely applied today. In the last decades, a large number of luminescent materials based on rare earth ions or rare earth host lattices have been invented. In many cases, rare earth phosphors dramatically improved the performance of the devices in which they are applied (Figure 4).

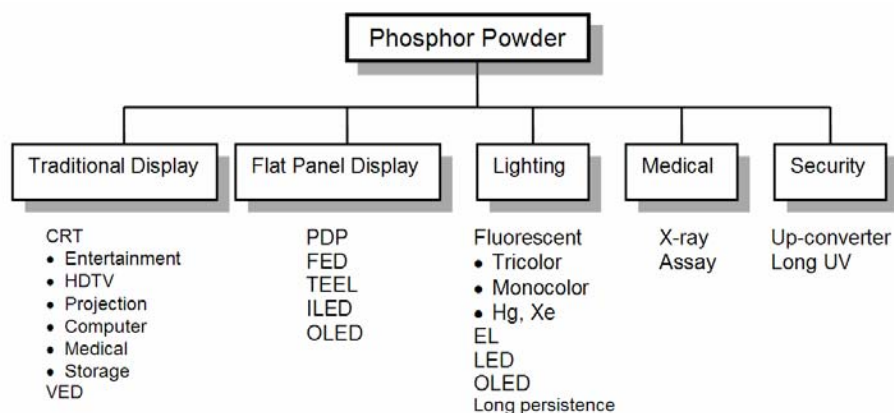


Figure 4. Major phosphor's applications.

Major applications of europium and terbium activated phosphors are in emissive displays and fluorescent lamps. Three types of flat luminescent displays are under development: plasma display panels, in which phosphor powders are excited by VUV photons (145-180nm); field emission displays, in which the luminescent material is bombarded by low-energy electrons emitted by microtips; and thin-film electroluminescence displays in which electrons injected into the luminescent layer are accelerated under the applied field up to the energies needed to excite luminescent centers [5-7].

A more specialized and important application is the use of X-ray intensifying screens for medical purposes [8]. Some X-ray detector systems are based on luminescent materials as well. Research on X-ray phosphors is mainly focused on photostimulable phosphors for digital imaging; the luminescence of which is obtained by optical excitation in an absorption band formed under X-ray irradiation [9]. Scintillator crystals convert the energy of ionizing radiations into UV or visible radiation. They are used for medical diagnostics, scientific experiments and industrial control (e.g., inspection of baggage and containers, thickness control of metal sheets, paper, geophysical exploration).

During the last ten years, white LEDs have become very important lighting sources and the importance of LED phosphors for white and coloured light generation must be considered an important market driver in the future [10-16].

4. Experimental Procedures

The examined materials for different applications were prepared by two methods: solid state reaction and combustion synthesis. The conventional solid state reaction is mostly used for preparation of bulk phosphors that used in traditional applications as safety signs, watch dials, decorative objects and toys. Combustion method is used for preparing nanoparticle materials which we need in medicine and sometimes in biology.

4.1. Solid state reaction

Strontium aluminate phosphor doped with Eu^{2+} and co-doped with Dy^{3+} ($\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$) for traditional applications were prepared by solid state reaction approach using strontium carbonate (SrCO_3 ; Aldrich, 99.9%), aluminum oxide (Al_2O_3) europium oxide (Eu_2O_3 ; Aldrich, 99.99%), and dysprosium oxide (Dy_2O_3 ; Aldrich, 99.99%) as the starting materials. Small amount (0.2mol%) of H_3BO_3 was used as a flux. Prior to heating at 1250°C , the reagents were ground using a ball mill to form a homogeneous mixture. First, the dry milling was used for 30 minutes and then continued by wet-mixing machine for 30 minutes. The resulting slurry was dried at 150°C for 3 hours to remove the water content. After fully dried, the mixed white powder was placed in a small alumina crucible and then fired at 1250°C for 2 hours under a mild reducing atmosphere. Graphite crucible was used to create the reducing atmosphere and to ensure complete reduction of Eu^{3+} to Eu^{2+} and to crystallize and form the luminescence centers. Usually the particle size in this process is about 10-20 micrometers. The mixing-milling process to get smaller particle size and homogeneous mixture was used after calcination.

4.2. Combustion synthesis

Similar nanoparticles of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ phosphor were prepared by combustion synthesis. The starting material included: Aluminium nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; System, 98%), strontium nitrate ($\text{Sr}(\text{NO}_3)_2$; Aldrich, 99%), europium oxide (Eu_2O_3 ; Aldrich, 99.99%), and urea ($\text{CO}(\text{NH}_2)_2$; System, 99%). Small amount of acid boric (H_3BO_3 ; Fisher, 100.04%) were used as flux and small amounts of urea were used as reducer and fuel. Figure 5 below shows the flow chart of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ powders synthesis.

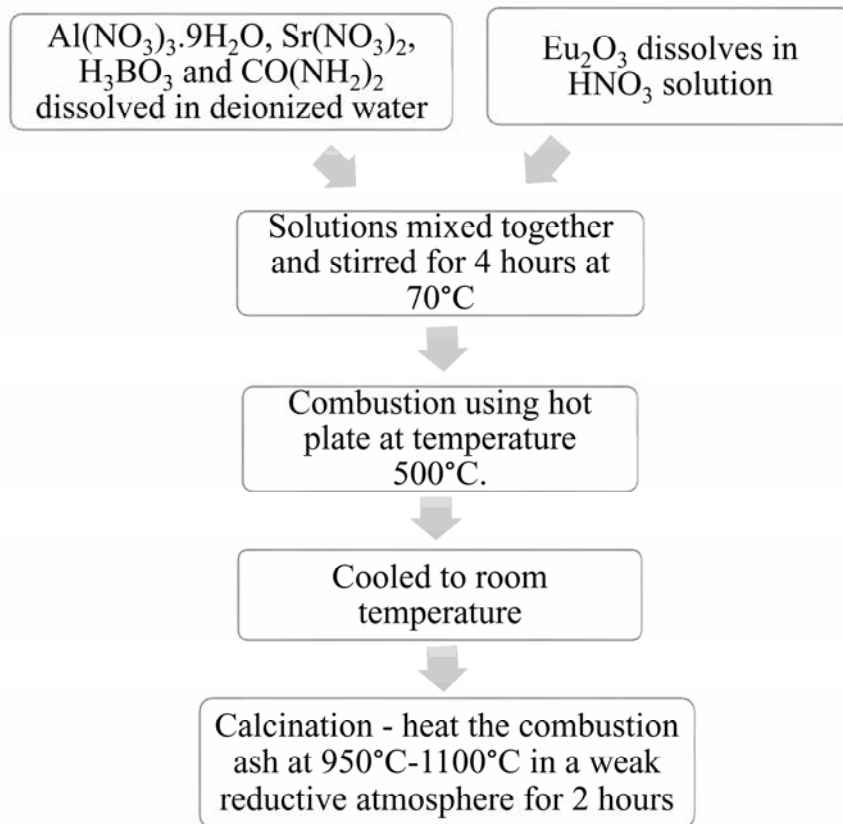
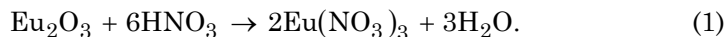


Figure 5. Flow chart of SrAl₂O₄:Eu²⁺ phosphors powder by combustion synthesis.

There are some details below to describe the combustion synthesis.

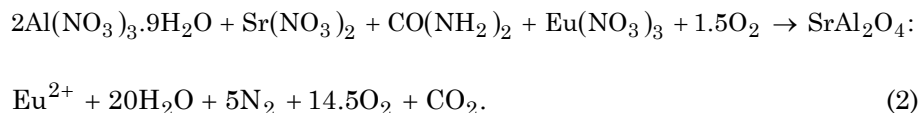
The stoichiometric quantities of raw materials were calculated and weighed by using high precision mass balance. The composition of the acid boric was set as 0.08mol%. Each raw materials Al(NO₃)₃·9H₂O, Sr(NO₃)₂, H₃BO₃, and CO(NH₂)₂ were dissolved into 20ml of deionized water respectively to obtain transparent solution. Wet mixing was used to obtain homogeneous mixture. Deionized water is selected instead of distilled water due to the removal of the mineral ions such as cations from sodium, calcium, iron, copper and anions from chloride and bromide

which will influence on the experiment result. Eu_2O_3 was dissolves with minimum amount HNO_3 solution to convert into $\text{Eu}(\text{NO}_3)_3$ according to the Equation (1).



The two solutions were mixed together and stirred by using magnetic bar for several hours at 75°C to obtain viscous gel solution. The mixing temperature is set at the range between 70°C to 80°C in this project due to several reasons. Firstly, according to the MSDS, Aluminium nitrate has quite low melting point (73°C) but high boiling point or decomposition temperature (135°C). Heating aluminium nitrate above its melting point encourage formation of homogeneous solution. Furthermore, it's able to dissolve acid nitric which has low boiling point (83°C).

The mixed viscous gel obtained continues for combustion reaction. In this project, combustion is done by using hot plate instead of using furnace. White combustion ash was obtained in 3-5 min by combusting the precursor gel at temperature 500°C . Initially, the solution boiled and underwent dehydration, followed by decomposition with emission of large amounts of gasses (oxides of carbon, nitrogen and ammonia). Later, the viscous gels spontaneously start to burn and burn slowly without flame (smouldering combustion), thus producing white fined powder. The whole process takes less than 5 minutes. When heated at 500°C , the powder was hold for a few minutes to ensure the combustion reaction was complete. The chemical equation of combustion is complicated and not yet verified; however, the brief equation can be shown as below:



Next, the combustion ash was cooled to room temperature.

The final pigments synthesis is done by heating the combustion ash at 950°C-1100°C in a weak reductive atmosphere for 2 hours to obtain $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ phosphor. The weak reductive atmosphere was created by using graphite crucible to inhibit further oxidation take place.

Other compositions of persistent phosphors were synthesized by similar methods.

Exciting by UV or sun light this phosphor shows bright blue-green luminescence (Figure 6).



Figure 6. Bright luminescence of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} based phosphor in the open air under sun light excitation.

5. Persistent Phosphors for Painting, Medical and Biological Applications

Applications of persistent luminescence phosphors are rapidly expanding from bulk materials visible to everyone (e.g., exit signalization

on airplane cabin floors) to high tech products. In this review, we consider traditional applications, such as painting, and more interesting and important applications in medicine and biology. We propose also a new direction in study and application these materials, namely, underwater investigations of persistent luminescence for an artificial reef and algae cultivation.

5.1. Painting

Persistent phosphors are a type of phosphors that have very long persistent afterglow emission. The phenomenon of afterglow is as follows. After the excitation source is turned off, emission from previously trapped electrons is still observed. The irradiation used may be UV, visible light, X-ray, gamma radiation as well as usual sun light.

The mechanism of long persistent phosphors' phosphorescence is basically a three-level electron transition mechanism, including a ground state, an excited state, and a meta-stable trapping state. Phosphorescence lifetime is usually longer than the lifetime at the excited state, and it depends on the trap depth and trapping/detrapping mechanism.

Persistent luminescence has been intriguing to people for hundreds of years. The situation drastically changed about 17 years ago when Matsuzawa et al. [17] discovered bright and long-lasting luminescence in $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$. In 1996, they reported a new type of long persistent phosphor $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ with a strong emission at 520nm (green), which is developed from a phosphor $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ found by Abbruscato in 1971 [18]. Takasaki et al. [19] reported similar results. They found an afterglow with both a far higher initial intensity and a much longer lifetime compared to traditional $\text{ZnS}:\text{Cu}, \text{Co}$. The persistence time of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ was extended to longer than 16h (reported persistent time varied with detection limits from 10 to 20h) after codoping with Dy^{3+} .

A short time later, a similar long persistent phosphor $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}$, Nd^{3+} was reported with a blue emission at 450nm [20]. These two phosphors drew considerable attention from many scientists because a 16-h persistent time could bring phosphorescence over a whole night [21-24]. Since then, long persistent phosphor becomes one of the major research areas in luminescence materials.

Some novel methods have been developed while people are developing new long persistent phosphor systems. These methods include co-doping with ions as electron traps, co-doping ions to create defects for defect related electron traps, persistent energy transfer, etc.

These investigations have led to a renewed research interest, and it promoted the use of these persistent phosphors in signalization, traffic signs, power switch, traffic police uniforms, luminous paints, glow-in-the-dark toys, decorative objects, emergency signage, watches and clocks, dials and displays, textile printing, medical diagnostics, and many other applications.



Figure 7. Blue, red, pink, violet, yellow, and green colours are possible in glow dark paint.

Phosphorescent paint is commonly called “glow-in-the-dark” paint. It is made from different phosphors, such as silver-activated zinc sulphide, or, more recently, doped strontium aluminate, and typically glows a pale green to greenish blue colour. The mechanism for producing light is similar to that of fluorescent paint, but the emission of visible light persists for some time after it has been exposed to light. Phosphorescent paints have a sustained glow which lasts for up to 12h after exposure to light, but will eventually fade over time.

This type of paint has been used to mark escape paths in aircraft and for decorative use, such as “stars” applied to walls and ceilings (Figure 8).



Figure 8. Glow-in-the-dark rocket, planets and stars wall stick.

Some other examples of glow-in-the-dark application are shown in Figures 9-12.



Figure 9. Hand-painted glow-in-the-dark blue Angelfish art magnet.



Figure 10. Luminescent paint by Pieter van den Bosch.

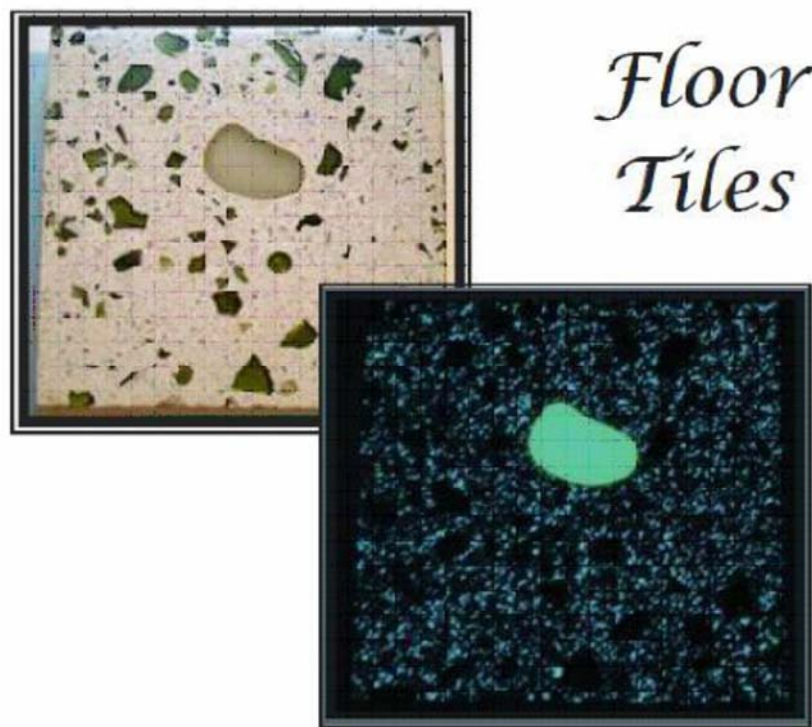


Figure 11. Decorative floor tiles.



Figure 12. A helmet and a high-voltage insulator (ceramic) in the day time and at dark.

5.2. Medical applications

With the development of high efficiency nanosized red phosphor, it has become possible to incorporate it in organic matrices to produce singlet oxygen, which kill cancer cells (Figure 13). This persistent phosphor is a very good candidate for photodynamic therapy (PDT) of cancer. Other light sources include light-emitting diodes (LEDs), which may be used for surface tumors, such as skin cancer [25]. Researchers continue to study ways to improve the effectiveness of PDT and expand its use to other cancers.

Over 2 mln people annually lost due to cancer. Photodynamic therapy has near 100% efficiency. PDT combines a drug (called a photosensitizer or photosensitizing agent) with a specific type of light to kill cancer cells. When photosensitizers are exposed to a specific wavelength of light, they produce a form of oxygen that kills nearby cells [26-32] (Figure 13). PDT may also be repeated and may be used with other therapies, such as surgery, radiation, or chemotherapy [28, 29].

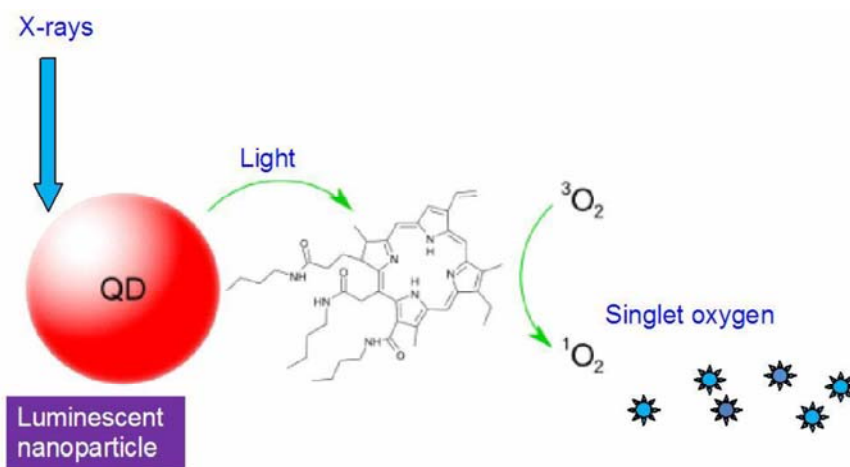


Figure 13. Cancer therapy using luminescent nanoparticles, which produces red light and then singlet oxygen when irradiated with X-rays.

Each photosensitizer is activated by light of a specific wavelength [30-34]. This wavelength determines how far the light can travel into the body [25, 30-32]. Thus, doctors use specific photosensitizers and wavelengths of light to treat different areas of the body with PDT.

In the first step of PDT for cancer treatment, a photosensitizing agent is injected into the bloodstream. The agent is absorbed by cells all over the body but stays in cancer cells longer than it does in normal cells. Approximately 24 to 72h after injection [26, 27], when most of the agent has left normal cells but remains in cancer cells, the tumor is exposed to light. The photosensitizer in the tumor absorbs the light and produces an active form of oxygen that destroys nearby cancer cells [26-32].

The light used for PDT in traditional application can come from a laser or other sources [25, 28, 29] (Figure 14).

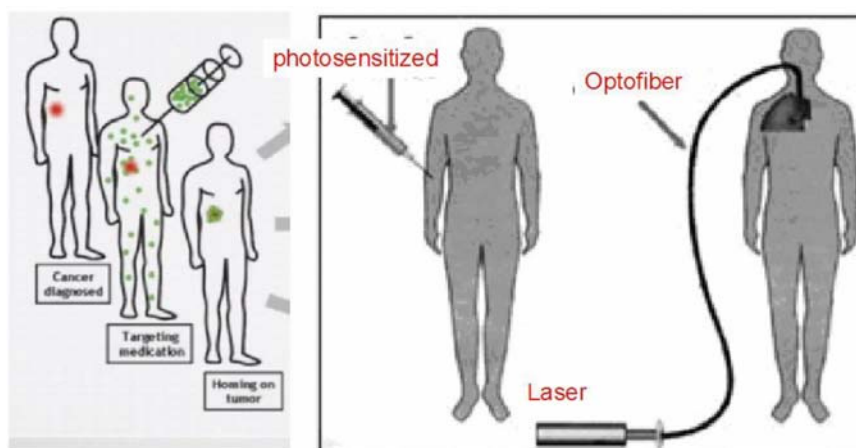


Figure 14. Laser light is directed through fiber optic cables.

Laser light can be directed through fiber optic cables (thin fibers that transmit light) to deliver light to areas inside the body [28, 29]. For example, a fiber optic cable can be inserted through an endoscope (a thin, lighted tube used to look at tissues inside the body) into the lungs or esophagus to treat cancer in these organs, but it is difficult in application for internal organs. Therefore, the cancer therapy using luminescent nanoparticles instead of optic cables seems to be promising and more

efficient. One of the aims of our work is to use a red persistent nontoxic nanosized phosphor exposed to X-ray inside the body as a new photosensitizer and produce a form of oxygen that kills nearby cancer cells.

5.3. Biological applications

There is a risk of forever damaging the existence of thousands natural reefs because of tsunami or other cataclastic phenomena. We need to know how to restore or sometimes to improve reefs and marine ecosystems. Therefore, measuring and interpreting the impact of human actions on the diversity on marine and oceanic life represent one way to prevent ecological disasters and predict possible environmental changes.

Artificial rock and block made of steel slag hybrid matrix were developed recently in Japan [35, 36]. Electric Arc Furnace (EAF) slag is the byproduct from steelmaking process with an estimated amount generated of about 10-15 weight percent (wt.%) for every ton of steel produced [37]. Steel slag is used in the production of cement [37], coastal marine blocks for seaweed bed [38] and substrate for mangrove rehabilitation [39]. Steel slag has also been shown to be effective in corral growing due to significant amount of calcium and silicon present in its composition [40]. Steel slag can be modified to form potassium calcium silicate (K_2CaSiO_4) [38]. This mineral has been of interest in the field of applied mineralogy due to the crystal structure which dissolves slowly in acidic soil providing valuable nutrients [41]. Its production from steelmaking slag is renewable resource and allows for greater waste recycling from steelmaking process. It can also be found in products such as the ashes from biomass combustion [42]. The production of this fertilizer is from iron slag after the desiliconization process of hot metal in the steel mill [38]. The main mineral phase present was $K_2Ca_2Si_2O_7$ [43]. However, researchers are yet to clarify the actual chemical composition of mineral phase present in this compound and mechanism of its dissolution as a fertilizer [42].

We propose experimental artificial glow reef to make from steel slag as well as from concrete and sand to provide hard surface. Other decision is to cover this artificial reef as well as real corals by persistent phosphors. The main goal of these experiments is to cultivate the algae in future and to attract the fishes. An artificial block from concrete and sand covered by $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} based phosphor was made and a new direction in study and application of persistent phosphors was proposed. For the first time, the underwater luminescence was experimentally studied in real sea conditions. Our pioneers works in this field were published recently [44, 45].

In this present study, Scheil-Gulliver model was applied to slag solidification to characterize the solidification behavior of mineral phase formation in a modified EAF slag system. Details of the solidification modeling have been described elsewhere [46]. In the experimental work, EAF slag from a Malaysian steel company was modified with 20wt.% K_2CO_3 . Each powder mixture was placed in an alumina crucible and melted in a Lenton EHF 1700 furnace. Details of the experimental work have been described elsewhere [47]. The plant chosen for the study was *Typhonium flagelliforme* or better known in Malay as “Keladi Tikus”. *Typhonium flagelliforme* is a medicinal herb plant that belongs to the Araceae family [48]. For the plant fertilization study, 3 conditions was investigated. These conditions were in a deionized water (DI) without fertilizer, DI with potassium silicate slag (PSS) fertilizer and DI with PSS coated by an epoxy layer with persistent $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$ phosphors. The phosphors coating was done to investigate the effect of fertilizer absorption due to enhance photosynthesis activity. Persistent phosphors can emit light for a long time from seconds to many hours after the excitation has ended. The irradiation used may be UV, visible light, X-ray, gamma radiation, as well as usual sun light.

The results of solidification model for slag system is given in Figure 15. For 0.6 CaO/SiO₂ wt. ratio, after complete solidification, six mineral phases were formed, with their percentage fraction given in Figure 15. Potassium silicates (PS) started to form at 650°C and reached a maximum composition of 27.5wt.% at 605°C where the solidification ends. Detailed analysis of effect of CaO/SiO₂ wt. ratio with respect to PS formed is given elsewhere [49].

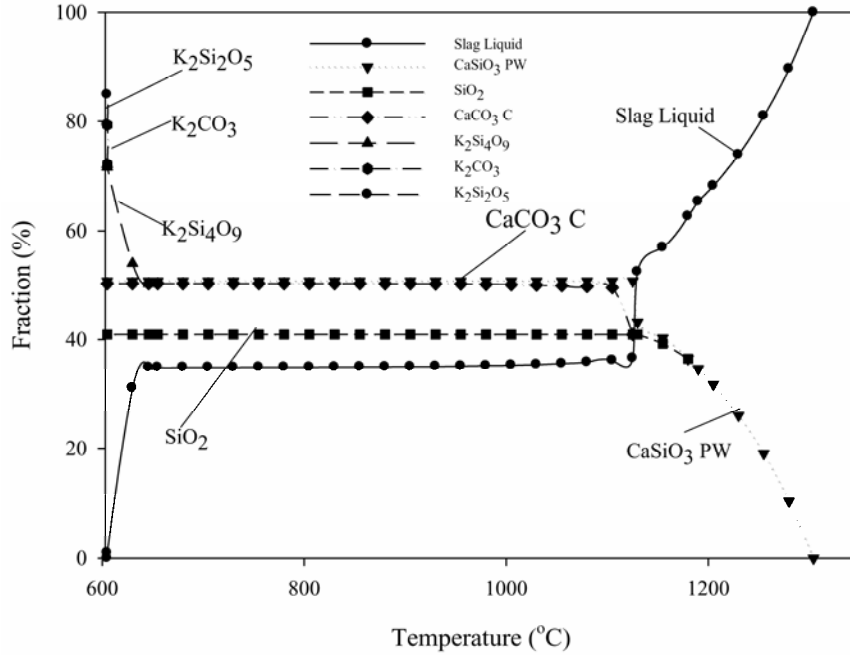


Figure 15. Fractions of simulated mineral phase during solidification at 1330°C-600°C (CaO/SiO₂ = 0.6).

The mineralogical compositions of the modified PSS samples were analyzed by XRD and shown in Figure 16. The diffraction patterns of the slags showed that there are heterogeneous materials consisting of mixtures of crystalline and amorphous phases. According to Figure 16, three crystalline phases were identified in the air cooled synthetic slag (EAF0A): potassium silicate (K₂Si₂O₅), silicon dioxide (SiO₂) and

alpha calcium silicate (α -CaSiO₃). In the water cooled synthetic slag (EAF0W), three crystalline phases were detected: alpha calcium silicate (α -CaSiO₃), potassium silicate (K₆Si₃O₉) and potassium calcium silicate (K₈CaSi₁₀O₂₅).

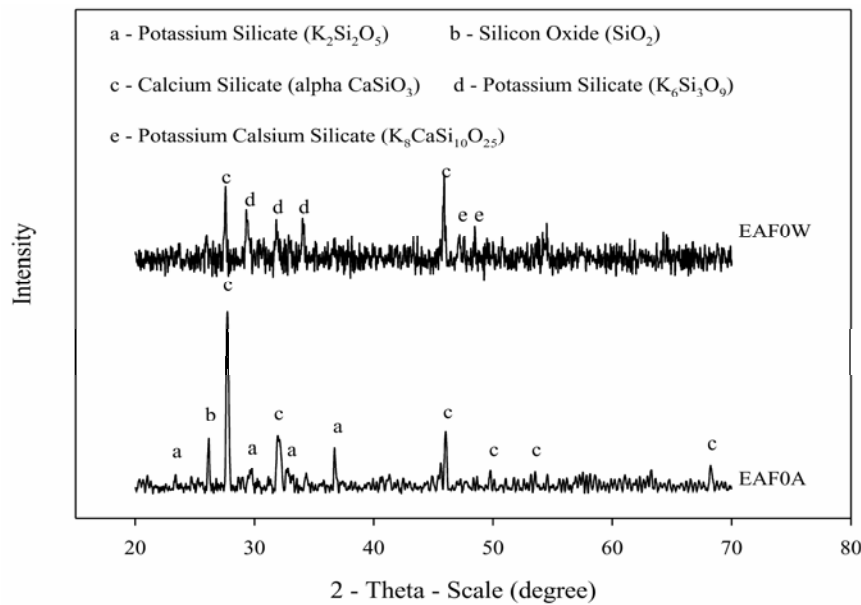


Figure 16. XRD pattern of modified synthetic EAF slags system. EAF0A = Air cooled with 0.6 wt. ratio of CaO/SiO₂ and EAF0W = Water cooled with 0.6 wt. ratio of CaO/SiO₂.

Initial plant fertilization study by PSS was investigated on *Typhonium flagelliforme* in DI water with different conditions. Figure 17 shows the pH relationship to different fertilization conditions. From Figure 17, the pH values increased within the first 24 hours in all plants before slowly settling to an optimum condition after 400 hours. Plants grown with DI only settled at a pH of 5, which is close to pH produced by 2wt.% of citric acid. The acidic nature of the *Typhonium flagelliforme* is well suited to the application of PSS [50]. This is due to the neutralization that will occur with the basic PSS. On the other hand, the plants with PSS and coated PSS fertilization settled at a basic pH. Both

conditions showed a similar trend in the pH values variation with time, settling at around 8.9 and 8.7. However, the coated PSS had a slightly lower pH value. This can be attributed to the phosphor coatings which slowed the release of nutrients from the PSS fertilizer. Future work will investigate the nitrogen, potassium, calcium, silicon, and phosphorus content of the leaves with respect to the fertilization conditions. It has been shown that a higher potassium and silicon uptake by plants is expected with PSS fertilization [51]. This in turn will lead to better plant growth and disease immunity [52].

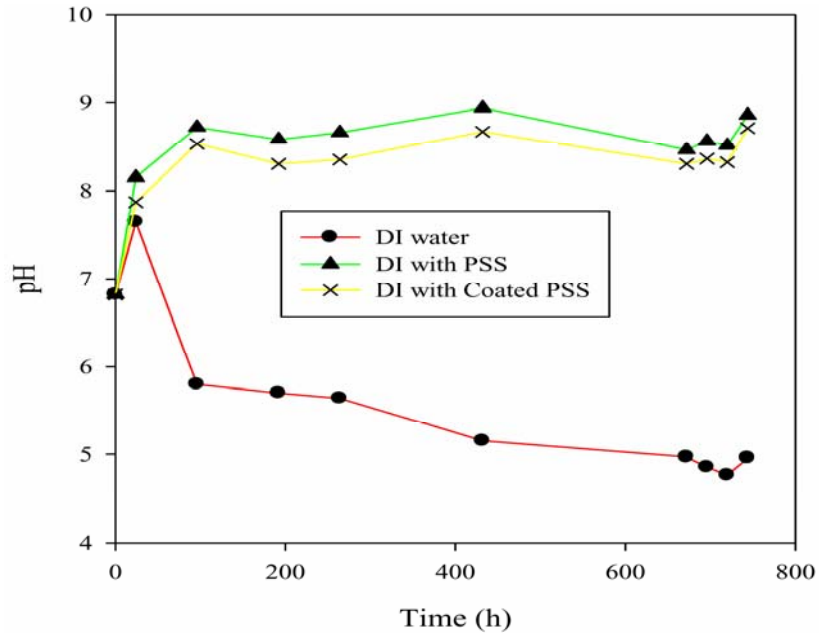


Figure 17. pH measurement of *Typhonium flagelliforme* with different fertilization condition.

5.4. Underwater luminescence

Below we show some applications of artificial reefs from metallic construction and slag with persistent phosphors in real sea conditions near the Malaysia in Indian Ocean.

The real underwater experiments in sea conditions were carried out in Pulau Payar, Malaysia. First, the artificial blocks covered by $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} and excited by the sun light were installed on the ocean floor with different relief (agropora corals, rocks, sand) and at different deep from 2 up to 6 meters. Figure 18 shows the process of installation artificial luminescent block on real stone in the sea at the deep about 5 meters.



Figure 18. Installation of concrete matrix covered by $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} .

Next step was the underwater luminescence investigations. All blocks showed the bright blue-green luminescence from all the places independently of relief and deep. One of the examples is demonstrated in Figure 19.



Figure 19. Blue-green colour luminescence of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ from 5 meters deep in real sea conditions.

After some minutes the fishes were interested in a new luminescent object and gathered around it (Figure 20).



Figure 20. The fishes are attracted by bright and long-lasting luminescence of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$.

Finally, the black-tip shark was also interested in luminescence and came near our artificial sample (Figure 21).



Figure 21. The black-tip shark is also interesting in luminescence.



Figure 22. Real coral on a metallic construction (Pulau Kapas).



Figure 23. Artificial coral reefs (Pulau Kapas).

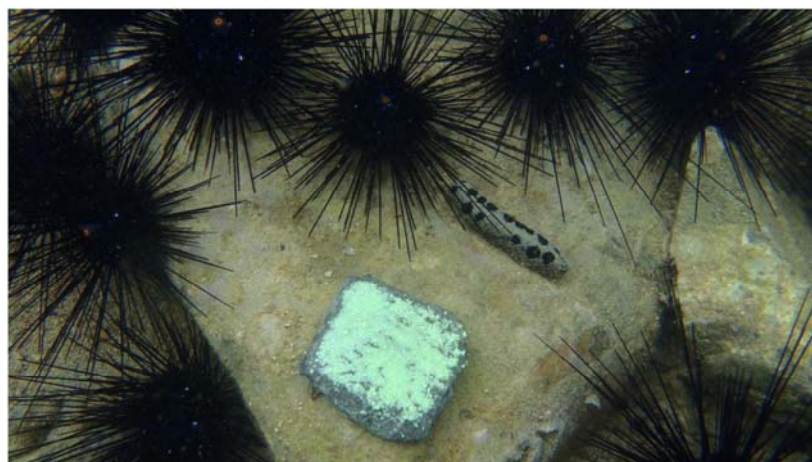


Figure 24. Green luminescence from slag covered by persistent $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ in sea-urchin environment.

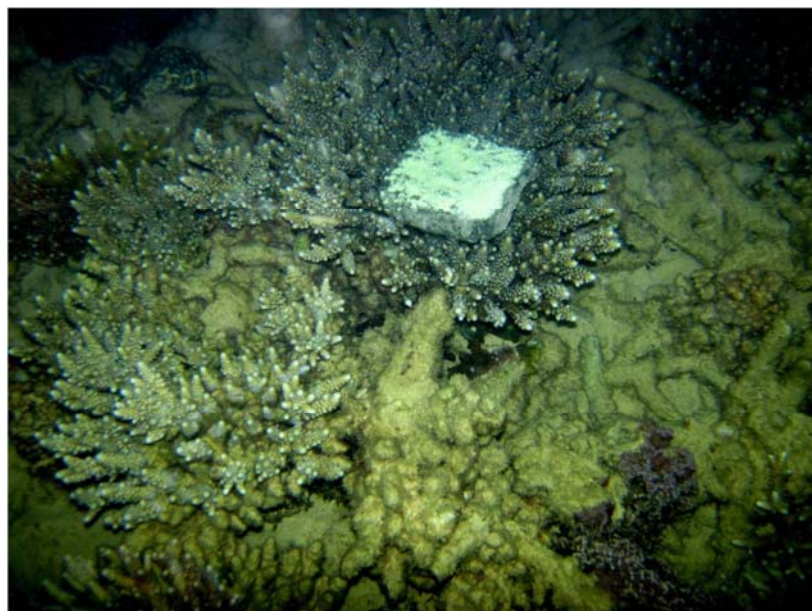


Figure 25. Artificial luminescent block inside real corals.



Figure 26. Real coral with phosphor inside.

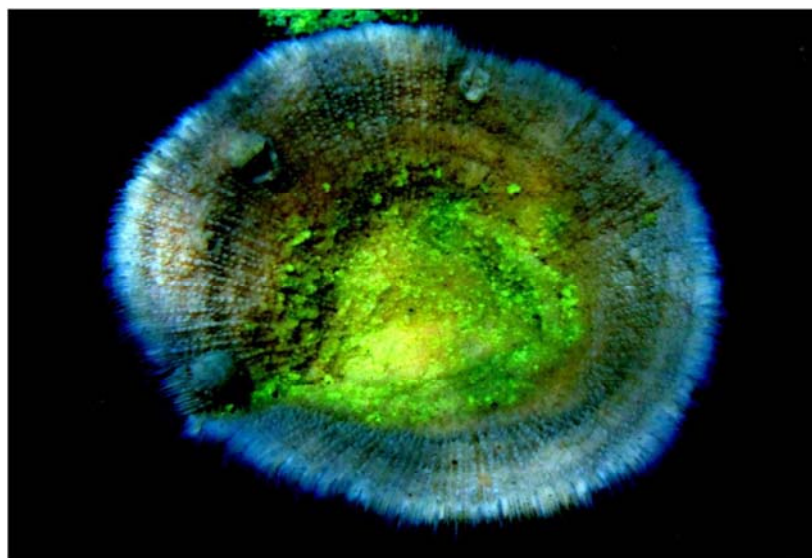


Figure 27. Night luminescence of real coral covered by phosphor.

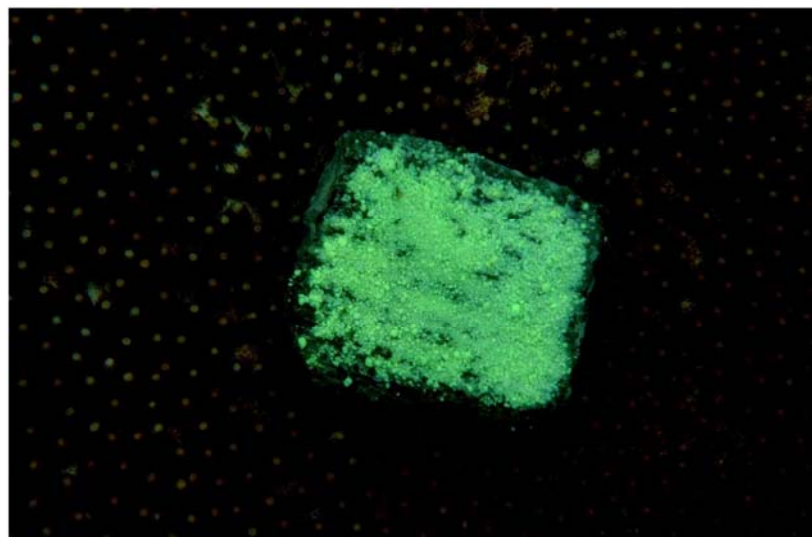


Figure 28. Night luminescence of artificial slag covered by phosphor.



Figure 29. The clown fishes are attracted by the bright light of artificial reef.

6. Conclusions

Short review is given to show the past and present of luminescent materials.

Major phosphor's applications in traditional display, flat panel display, lighting, medical, security are presented.

Multiphase micro and nanoparticle blue-green persistent phosphor with turquoise luminescence was synthesized and applied for painting, medical and biological investigations.

A lot of examples show a very large range of applications of persistent luminescence phosphors from bulk materials visible to everyone to high tech products, especially in medicine. The development of high efficiency nanosized phosphor gives the possibility to incorporate it in an organic matrix to produce singlet oxygen, which kill cancer cells. This persistent phosphors are very good candidates for photodynamic therapy of cancer.

For the first time, the experiments with an artificial stone covered with $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} based phosphor were carried out under real sea conditions in Pulay Payar Marine Park Malaysia. Strong, and bright blue-green (turquoise) luminescence was observed and registered under water.

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