UNDERWATER LUMINESCENCE OF $SrAl_2O_4:Eu^{2+}$, Dy^{3+} PERSISTENT PHOSPHOR

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Abstract

An artificial block from concrete and sand covered by $SrAl_2O_4:Eu^{2+}$, Dy^{3+} based phosphor was prepared, and a new direction in the study and application of persistent phosphors was proposed. For the first time, underwater luminescence was experimentally studied in real sea conditions. The bright blue-green long-lasting afterglow was demonstrated and registered from a depth of 5 m. The fishes were attracted by the light of the artificial reef.

1. Introduction

Persistent phosphors can emit light for a long time from a few 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.

Persistent luminescence has intrigued people for hundreds of years. The situation drastically changed about 16 years ago when Matsuzawa *et al.* discovered bright and long-lasting luminescence in $SrAl_2O_4$:Eu,Dy [1]. By codoping the green-emitting phosphor $SrAl_2O_4:Eu^{2+}$ (already showing a relatively strong and long-lasting afterglow by itself [2]) with the rare earth element dysprosium (Dy^{3+}), they were able to create a material that emitted bright light for hours after ending the excitation (simultaneously and independently, Takasaki *et al*. reported similar results [3]). They found an afterglow with both a far higher initial intensity and a much longer lifetime compared to traditional ZnS:Cu,Co. These investigations have led to a renewed research interest, and it promoted the use of these green-emitting persistent phosphors in signalization, glow-in-the-dark toys, emergency signs, dials and displays, textile printing, medical diagnostics, and many other applications. Applications of persistent luminescence phosphors are rapidly expanding.

In this article, we propose a new direction in study and application these materials, namely underwater investigations of persistent luminescence. A new multiphase blue-green phosphor based on $SrAl_2O_4$ was synthesized and applied in real sea conditions.

2. Experimental procedures

2.1. Sample preparation

An artificial rock and block made of a steel slag hybrid matrix have been recently developed in Japan [4, 5]. We propose to prepare an experimental artificial glow reef from concrete and sand to provide a hard surface. Another decision is to cover the real corals by persistent phosphors. The main goal of these experiments is to cultivate the algae in the future

and to attract the fish. For this purpose, the artificial block must be luminescent and preferably excite the green light. The $SrAl_2O_4:Eu^{2+}$, Dy^{3+} persistent phosphor as a phosphorescence material and polymer epoxy as a coating layer are proposed. Strontium aluminate phosphor doped with Eu^{2+} and co-doped with Dy^{3+} $SrAl_2O_4:Eu^{2+}$, Dy^{3+} were prepared by a 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 starting materials. A small amount (0.2 mol %) of H_3BO_3 was used as a flux. Prior to heating at 1250ºC, the reagents were ground using a ball mill to form a homogeneous mixture. First, the dry milling was used for 30 min and then continued using a wet-mixing machine for 30 min. The resulting slurry was dried at 150°C for 3 h 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 h under a mild reducing atmosphere. A 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. The mixing–milling process to get a smaller particle size and a homogenous mixture was used after calcination. This phosphor excited by UV or sun light shows bright blue-green luminescence (Fig. 1).

Fig. 1. Bright luminescence of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} based phosphor in the open air under sun light excitation.

In this study, an epoxy layer of the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphor was deposited on the reef surface by a brushing technique. A certain amount of mixed polymers Epoxy DEN 431 and polyetheramine D230 hardener was prepared, and 30–40 wt% of the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphor pigment were added to produce a high glowing intensity. After precise weighing of all materials, the slip mixture was manually mixed to a homogeneous composition of the epoxy solution and phosphor pigments. This solution was applied on the reef surface by a brushing technique with controlled thickness of the coating layer. The surface interactions between the epoxy layer of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} and reef took place during the curing process at 100ºC for 1 h. The final artificial block and coral are shown in Fig. 2.

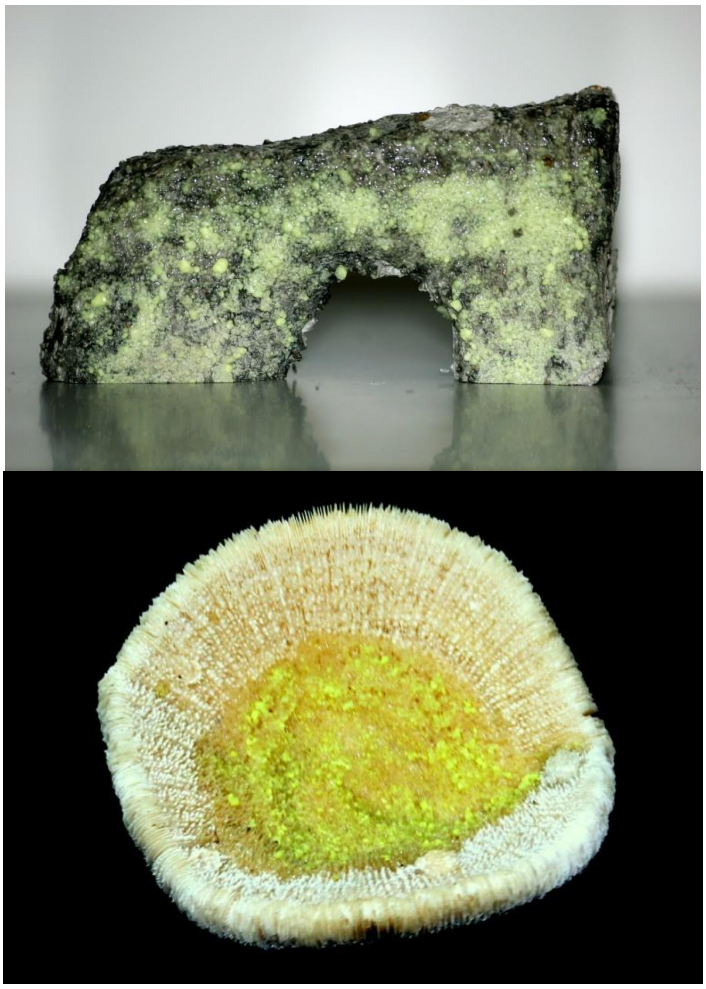

Fig. 2. Artificial block from concrete and sand covered by $SrAl_2O_4:Eu^{2+}$, Dy^{3+} (top) and real coral with phosphor inside (bottom)

The persistent effect or long-lasting afterglow luminescence is seen in Fig. 3. The phosphor inside the coral was excited by the sun light in the daytime and shows very bright green luminescence in the night.

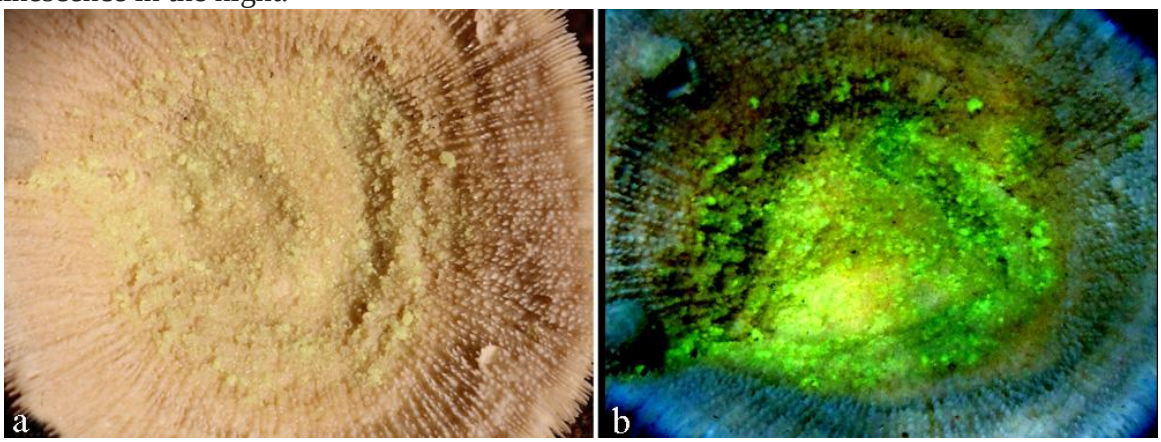

Fig. 3. Day (a) and night (b) luminescence of $SrAl_2O_4:Eu^{2+}$, Dy^{3+}.

2.2. Sample characterization

The morphology and structure of the as heated products were studied by an XRD Bruker, D8 Advance X-ray Diffractometer with Cu-Kα radiation at a wavelength of 1.54 Å. Data have been collected by step-scanning 2θ from 10 to 90° and 0.034 s counting time at each step at room temperature.

The photoluminescence excitation and emission spectra were recorded using a Horiba Jobin Yvon IHR 550 UV Fluorescence Spectrometer. All the samples were excited by 325-nm radiation from a 450 W pulsed Xenon lamp.

No single method (XRD or PL) can supply the necessary information, which is now required for detailed analysis. The microscopic properties of synthesized materials are often caused by inhomogeneities on a microscopic scale. We have also chosen some of the traditional and some original modes and image processing to illustrate these possibilities. The luminescence properties were investigated with a modified Stereoscan SEM with an additional attachment for the color cathodoluminescence (CCL) mode [6]. CCL techniques used in conjunction with SEM can give both spectral and spatial information with high resolution. We used a recording system consisting of three multipliers with different light filters (R, G, B) and of a multichannel device connected with photomultipliers. It allows simultaneous transmission of video signals on all channels in any pre-determined range of the spectrum. Images of the surface under study and the corresponding CL emission from the surface were displayed on video monitors. The CL images can be recorded with the total emitted integral (panchromatic) CL as well as with light of fixed spectral wavelength by using a suitable photodetector. The combination with the secondary electron image with the backscattered electrons allows the analytical CL image to be compared with the surface topography of the sample. To avoid charging effects, all the samples were coated with a thin conductive aluminum layer (about 100 Å) before the SEM examinations.

3. Results and discussion

3.1. Structure, morphology, and luminescence

Figure 4 shows the XRD patterns of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} annealed at 1250°C for 2 h in an active carbon atmosphere.

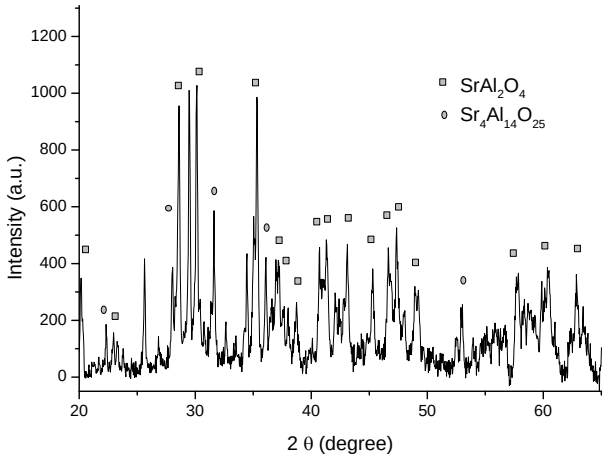

Fig. 4. XRD patterns of the synthesized phosphor.

From Fig. 4, it is seen that the XRD patterns include two phases $SrAl_2O_4$ and $Sr_4Al_{14}O_{25}$, indicating the formation of mixed oxide phases. As the firing temperature is raised to 1250°C, the XRD peaks become sharper and stable phases of $SrAl_2O_4$ and $Sr_4Al_{14}O_{25}$ with higher crystallinity can be obtained.

PL spectroscopy indirectly confirms the presence of two phases. The detailed results of these experiments are given in our previous articles [7-9]. Here in Fig. 5 we show the emission spectra of synthesized phosphor.

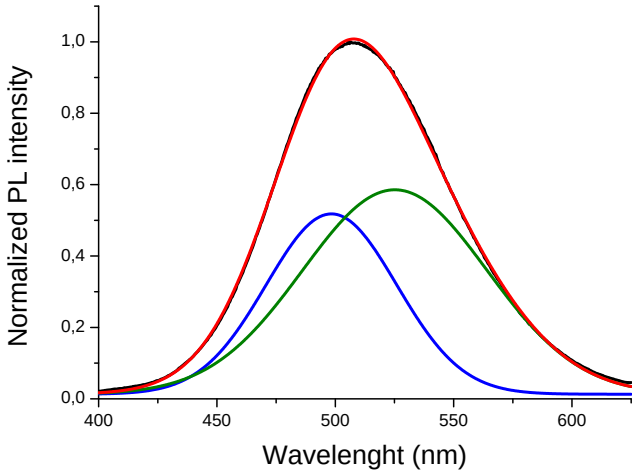

Fig. 5. Decomposition of total PL intensity on blue and green bands.

The asymmetry of PL emission intensity allows us to decompose this spectrum into blue and green bands peaked around 490 and 520 nm. These bands correspond to $Sr_4Al_{14}O_{25}$ (490 nm) and $SrAl_2O_4$ (520 nm) phases doped with Eu^{2+}.

A direct confirmation of this hypothesis follows from cathodoluminescence measurements. The results of experimental investigations of the prepared phosphors by secondary electrons and color cathodoluminescence, as well as combined signal, are presented in Fig. 6. In all experiments, the accelerating voltage in SEM was 20 kV and the beam current 100 nA. The diameter of the electron beam did not exceed 0.1 μm. We used a recording system consisting of three multipliers with different light filters (R, G, B) and a multichannel device connected with photomultipliers. It allows simultaneous transmission of video signals on all channels in any pre-determined range of the spectrum. Images of the surface under study and the corresponding CL emission from the surface were displayed on video monitors.

In secondary electrons (Fig. 6a) we can see only the topography of agglomerated powder. CCL (Fig. 6b) shows the spatial distributions of different CL spectral bands (green 520 nm and blue 490 nm) belonging to $SrAl_2O_4:Eu^{2+}$, Dy^{3+} and $Sr_4Al_{14}O_{25}:Eu^{2+}$, Dy^{3+}, respectively. This direct experiment really confirms the existence of two different phases with different colors. Moreover, the absence of red color centers proves that all Eu^{3+} was reduced to Eu^{2+} in synthesis process. The combination of CCL with the secondary electron image (Fig. 6c) allows the analytical CL image to be compared with the surface topography of the sample.

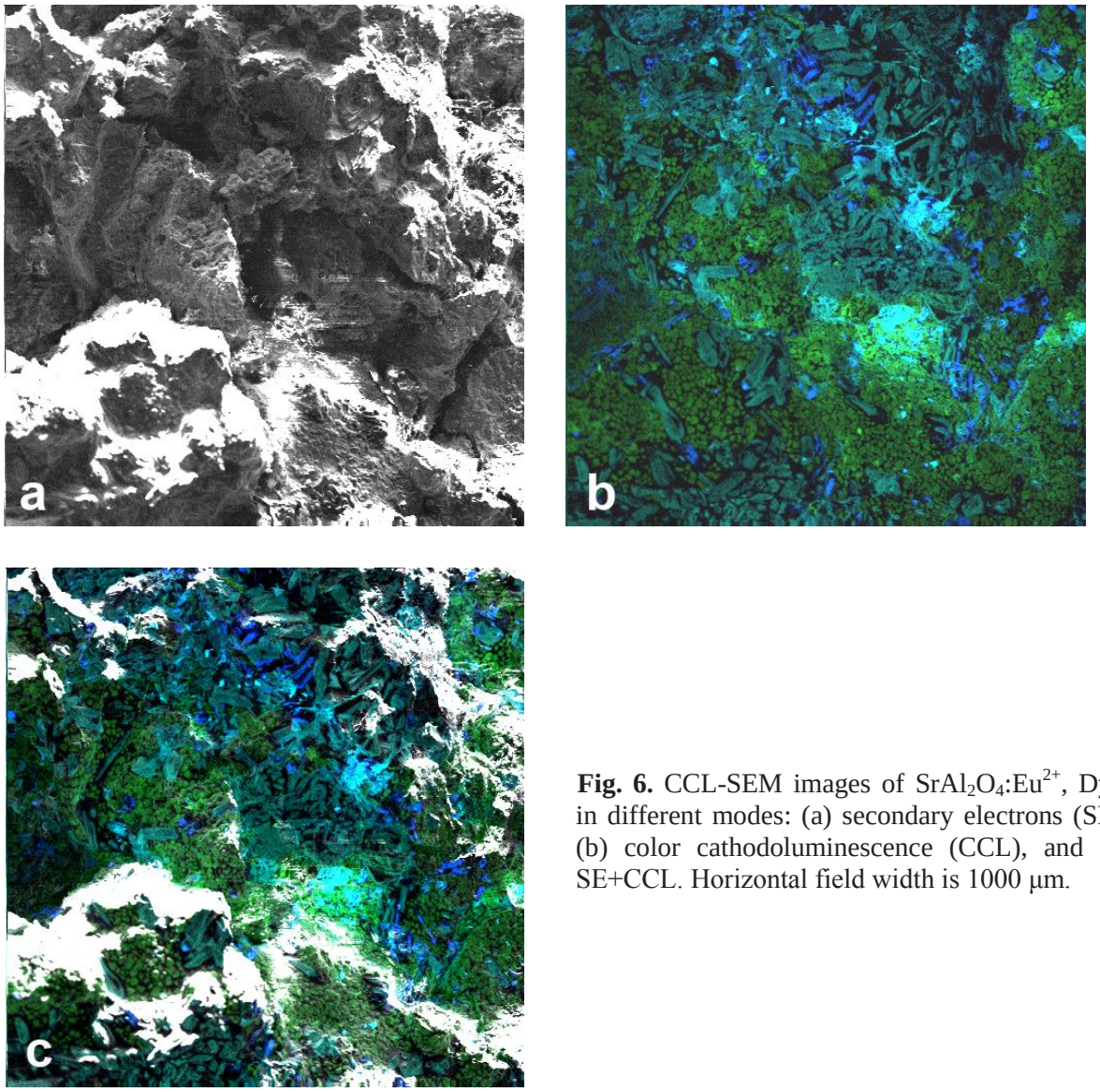

Fig. 6. CCL-SEM images of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} in different modes: (a) secondary electrons (SE), (b) color cathodoluminescence (CCL), and (c) SE+CCL. Horizontal field width is 1000 μm.

3.2. Underwater phosphor application

The first experiments with underwater luminescence were carried out in a room aquarium. Two glass cans with the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphor were installed near the surface and on the bottom of the aquarium. The left can was illuminated by the visible light, and the phosphor was excited in comparison with the right one (Fig. 7).

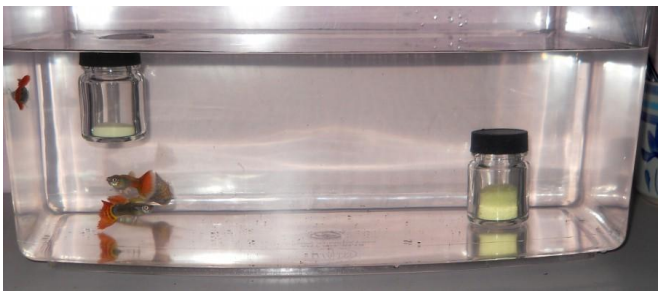

Fig. 7. Aquarium with excited (left) and nonexcited (right) phosphors.

The experiments show that the aquarium fishes mostly prefer to stay in the left part of the aquarium near the luminescent phosphor.

The real underwater experiments in sea conditions were carried out in Pulau Payar and Pulau Kapas, Malaysia. First, the artificial blocks covered by $SrAl_2O_4:Eu^{2+}$, Dy^{3+} and excited by the sun light were installed on the ocean floor with different relief (agropora corals, rocks, sand) and at different depth of 2 to 6 m. Figure 8 shows the process of installation of the artificial luminescent block on a real stone and corals in the sea at a depth of about 5 m.

Fig. 8. Installation of a concrete matrix covered by $SrAl_2O_4:Eu^{2+}$, Dy^{3+} on the stone (top) and on the real corals (bottom).

The next step was underwater luminescence investigations. All blocks showed the bright blue-green luminescence from all the places regardless of relief and depth. One of the examples is demonstrated in Fig. 9.

Fig. 9. Blue-Green color luminescence of an artificial concrete rock and a real coral covered by $SrAl_2O_4:Eu^{2+},Dy^{3+}$ from a depth of 5 m in real sea conditions

After some minutes, the fishes were interested in a new luminescent object and gathered around it (Fig. 10).

Fig. 10. The fishes are attracted by bright and long-lasting luminescence of $SrAl_2O_4:Eu^{2+}$, Dy^{3+}.

Fig. 11. Concrete matrix inside of Tridacna.

Finally, the black-tip shark was also interested in luminescence and came near our artificial sample (Fig. 12).

Fig. 12. The black-tip shark is also interested in luminescence

4. Conclusions

A multiphase blue-green persistent phosphor with turquoise luminescence was synthesized and applied for sea investigations. For the first time, the experiments with an artificial stone and coral covered by the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} based phosphor were carried out in real sea conditions in Pulau Payar Marine Park and Pulau Kapas Malaysia. Strong and bright turquoise luminescence was observed and registered under the water. The fishes were attracted by the light of the artificial reef.

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