A marine reef application for SrAl$_2$O$_4$:Eu Dy-based persistent luminescence phosphors

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INTRODUCTION
Persistent phosphors can emit light for a long time from seconds to many hours after the excitation has ended. The excitation irradiation for this form of luminescence may be ultraviolet, visible, X-ray or gamma radiation, as well as the usual sunlight.

Persistent luminescence has intrigued people for hundreds of years. The situation changed dramatically about 16 years ago when Matsuzawa et al. [1] discovered bright and long-lasting luminescence in the compound SrAl$_2$O$_4$:Eu,Dy. By co-doping the green-emitting phosphor SrAl$_2$O$_4$:Eu$^{2+}$ (which alone already shows a relatively strong and long-lasting afterglow [2]) with the rare earth element dysprosium (Dy$^{3+}$), they were able to create a material that emitted bright light for hours after the excitation ended. Simultaneously and independently, Takasaki et al. [3] reported similar results. 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, and medical diagnostics. The applications of persistent luminescence phosphors are rapidly expanding.

In this article we propose a new direction in the study and application of these materials namely underwater investigations of persistent luminescence. A new multiphase blue-green phosphor based on SrAl$_2$O$_4$ was synthesized and applied in marine conditions in the development of an artificial luminescent reef.

MATERIALS AND METHODS

SAMPLE PREPARATION
Artificial rocks and blocks made of a steel slag hybrid matrix were recently developed in Japan [4, 5]. We set out to make an experimental artificial glow reef from concrete and sand to provide a hard surface. The main goal of these reefs was to allow the future cultivation of algae to attract the fish. For this purpose the artificial block must be luminescent and preferably emit green light. We proposed to use the persistent phosphor SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ as a phosphorescent material and a polymer epoxy as a coating layer.

Strontium aluminate phosphor doped with Eu$^{2+}$ and co-doped with Dy$^{3+}$ (SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$) were prepared by a solid-state reaction method using strontium carbonate (SrCO$_3$, Aldrich, 99.9 %), aluminum oxide (Al$_2$O$_3$, europium oxide (Eu$_2$O$_3$, Aldrich, 99.99 %) and dysprosium oxide (Dy$_2$O$_3$, Aldrich, 99.99 %) as the starting materials. A small amount (0.2 mol %) of H$_3$BO$_3$ was used as a flux. Prior to heating at 1280°C, the reagents were ground up using a ball mill to form a homogeneous mixture. At first, dry milling was used for 30 minutes and was then followed by treatment in a wet-mixing machine for 30 minutes. The resulting slurry was dried at 150°C for 3 hours to remove the water content. When fully dried, the mixed white powder was placed in a small alumina crucible and then fired at 1280°C for 2 hours 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. A further mixing and milling process was used after calcination to get smaller particle sizes and a homogenous mixture. Under excitation by UV or sunlight this phosphor shows bright blue-green luminescence (Figure 1).

In this study, an epoxy layer of SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphor was deposited on the reef surface by a brushing technique. A mixture of the polymers Epoxy DEN 431 and hardener polyetheramine D230 was prepared and 30-40 wt% of SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphor pigment was added to produce a material with a high glowing intensity. After precise weighing of all materials, the slip mixture was manually mixed to homogeneous the composition epoxy solution and phosphor pigments. This solution was

Figure 1
Bright blue-green luminescence of SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ based phosphor in the open air with excitation by sunlight.

Figure 2
Artificial luminescent reef: a block made from concrete and sand covered by the SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ based phosphor.
applied to the artificial reef surface by a brushing technique which controlled the thickness of coating layer. The interaction of the epoxy layer of SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ and the reef surface took place during a curing process at 100ºC for 1 h. The final artificial block is shown in Figure 2.

**SAMPLE CHARACTERIZATION BY X-RAY DIFFRACTION, PHOTOLUMINESCENCE, SCANNING ELECTRON MICROSCOPY AND CATHODOLUMINESCENCE**

The morphology and structure of the as-heated products were examined by X-ray diffraction using a Bruker D8 advanced X-ray diffractometer with Cu-Kα radiation at a wavelength of 1.54 Å. Data were collected by step-scanning 2θ from 10° to 90° with a 0.034 second 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 exited by 325 nm radiation from a pulsed 450 W xenon lamp.

The morphological and structural properties of synthesized materials are often caused by inhomogeneities on a micron scale. So in addition to XRD and PL we used secondary electron and cathodoluminescence imaging in an SEM, and image processing to investigate these microscopic properties.

The samples were examined in a Stereoscan SEM equipped with an attachment for the colour cathodoluminescence (CCL) analysis [6]. To avoid charging effects, all the specimens were coated with a thin conductive aluminum layer (about 100 Å) before the SEM examination.

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.

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 photomultipliers with different light filters (R, G, B) and a multichannel device connected to photomultipliers. This allowed 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 were recorded with the total emitted integral (panchromatic) CL as well as with light of fixed spectral wavelength by using a suitable photodetector. By combining the CL signal with the secondary electron or backscattered electron images we were able to correlate the CL image with the surface microtopography of the sample.

**RESULTS AND DISCUSSION**

**STRUCTURE, MORPHOLOGY AND LUMINESCENCE**

Figure 3 shows the main XRD patterns of SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ annealed at 1250°C for 2 h in an active carbon atmosphere.

From Figure 3 it can be seen that the XRD patterns include two phases, SrAl$_2$O$_4$ and Sr$_4$Al$_3$O$_{12}$, indicating the formation of mixed oxide phases. When the firing temperature was raised to 1250°C, the XRD peaks became sharper showing that stable phases of SrAl$_2$O$_4$ and Sr$_4$Al$_3$O$_{12}$ with higher crystallinity could be obtained.

PL spectroscopy indirectly confirmed the presence of two phases. The detailed results of these experiments are given in our previous articles [7-9]. Here in Figure 4 we show the emission spectra of synthesized phosphor. The asymmetry of the PL emission intensity allowed us to decompose this spectrum into blue and green bands. These bands correspond to Sr$_4$Al$_3$O$_{12}$ (490 nm) and SrAl$_2$O$_4$ (520 nm) phases, doped by Eu$^{2+}$.

Direct confirmation of this hypothesis followed from the cathodoluminescence measurements. The results of our experimental investigations of prepared phosphors by secondary electron imaging and color cathodoluminescence as well as from the combined signal are presented in Figure 5.

In secondary electron imaging (Figure 5a) we can see only the topography of agglomerated powder. CCL (Figure 5b) shows the spatial distributions of different CL spectral bands (green 520 nm and blue 490 nm) belonging to Sr$_4$Al$_3$O$_{12}$:Eu$^{2+}$, Dy$^{3+}$ and SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$, respectively. This direct experiment really confirmed the existence of two different phases with different colours. Moreover, the absence of red color centers proves that all Eu$^{2+}$ was reduced to Eu$^{3+}$ during the synthesis process. The combination of CCL with the secondary electron image (Figure 5c) allowed the analytical CL image to be compared with the surface topography of the sample.

**UNDERWATER APPLICATION OF THE PERSISTENT PHOSPHOR**

The real underwater experiments in marine conditions were carried out in the sea at Pulau Payar Marine park in Malaysia. First, the artificial blocks coated with the new phosphor SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ which would be excited by sunlight were installed in regions of the sea floor with different relief (e.g. agropora corals, rocks and sand) and at different depths from 2 up to 6 meters. Figure 6 shows the process of installation of an artificial luminescent block on a real rock in the sea at a depth of about 5 meters.

Our next step was the investigation of underwater luminescence. All blocks showed the bright blue-green luminescence from all the places independent of their relief and depth. Two of the luminescing blocks are shown in Figure 7, in sunlight and at night. After some minutes the fishes were interested in this new luminescent object and gathered around it (Figure 8). Figure 8b shows a black-tip shark that was also interested in the luminescence of the reef.
CONCLUSIONS
Multiphase blue-green persistent phosphor with turquoise luminescence was synthesized and applied for sea investigations. For the first time the experiments with artificial stone covered by SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ based phosphor were carried out in real sea conditions in Pulay Payar Marine Park Malaysia. Strong and bright blue-green (turquoise) luminescence was observed and registered under the water. Fishes were attracted by the light of the artificial reef.

REFERENCES
BIOGRAPHY
Mihail Nazarov received his PhD degree in physics from the Physical Faculty of Moscow State University in 1973. He was an associate professor at the Technical University of Moldova, and a professor of physics in Annaba State University, Algeria (1979-1982). Later he worked in South Korea as a visiting professor at Korea Advanced Institute of Science and Technology (KAIST), principal researcher at Samsung CO, and a research professor at Dept of Materials Science & Engineering at Gwangju Institute of Science and Technology. He is now a visiting professor at Universiti Sains Malaysia. His research interests in the last years are in the developing new phosphors for flat panel display applications, solid state lighting and LEDs.

ABSTRACT
An artificial block from concrete and sand covered by SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ based phosphor was made 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. A bright blue-green long-lasting afterglow was demonstrated and registered from 5 meters deep. Fishes were attracted to the light of this artificial reef.

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Figure 8
(a) Fishes were attracted by the bright and long-lasting luminescence of the SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ coated blocks. (b) A black-tip shark was also interested in the luminescence.