Research Article

Photocatalytic Activity and Optical Properties of Blue Persistent Phosphors under UV and Solar Irradiation

C. R. García,^{1,2} L. A. Diaz-Torres,¹ J. Oliva,¹ M. T. Romero,² and P. Salas³

¹Laboratorio de Fotocatálisis y Fotosíntesis Artificial, Centro de Investigaciones en Óptica, AP 1-948, 37150 León, GTO, Mexico

²Facultad de Ciencias Físico Matemáticas, Universidad Autónoma de Coahuila, Camporredondo, 25000 Saltillo, COAH, Mexico

³Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México, AP 1-1010, 76000 Juriquilla, QRO, Mexico

Correspondence should be addressed to L. A. Diaz-Torres; ditlacio@cio.mx

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Blue phosphorescent strontium aluminosilicate powders were prepared by combustion synthesis route and a postannealing treatments at different temperatures. X-ray diffraction analysis showed that phosphors are composed of two main hexagonal phases: SrAl_2O_4 and $\text{Sr}_3\text{Al}_{32}\text{O}_{51}$. The morphology of the phosphors changed from micrograins (1000°C) to a mixture of bars and hexagons (1200°C) and finally to only hexagons (1300°C) as the annealing temperature is increased. Photoluminescence spectra showed a strong blue-green phosphorescent emission centered at $\lambda_{\text{em}} = 455 \text{ nm}$, which is associated with $4f^6 5d^1 \rightarrow 4f^6 (^8S_{7/2})$ transition of the Eu^{2+} . The sample annealed at 1200°C presents the highest luminance value (40 Cd/m^2) with CIE coordinates (0.1589, 0.1972). Also, the photocatalytic degradation of methylene blue (MB) under UV light (at 365 nm) was monitored. Samples annealed at 1000°C and 1300°C presented the highest percentage of degradation (32% and 38.5%, resp.) after 360 min. In the case of photocatalytic activity under solar irradiation, the samples annealed at 1000°C, 1150°C, and 1200°C produced total degradation of MB after only 300 min. Hence, the results obtained with solar photocatalysis suggest that our powders could be useful for water cleaning in water treatment plants.

1. Introduction

Long persistent phosphor (LPP) materials have several applications such as emergency signals in the darkness, wall painting, radiation detection, displays, lamps, and decorations [1]. Due to their importance, the development of new LPP with stable chemical and physical properties is still a challenge in the field of materials science. Long persistent $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ (510 nm) phosphors have shown high brightness lasting for 10 h [2, 3]. Similarly, blue phosphorescent emission at around $\lambda_{\text{em}} = 450 \text{ nm}$ has been obtained from $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ (430 nm), $\text{SrMgSi}_2\text{O}_6:\text{Dy}^{3+}$ (455 nm), and $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}, \text{Co}^{3+}$ (450 nm) systems [1, 4]. Nonetheless, these systems showed less brightness and time of phosphorescence than those for the green $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor. Thus, the development of new blue LPPs materials with blue emission at around 450 nm is required for the applications mentioned above.

Besides, few reports have demonstrated the use of the LPPs in the photocatalysis area. It has been proposed that the mixture of LPPs and photocatalyst composites can help to improve the photocatalytic process under ultraviolet (UV) light excitation: The photocatalyst/LPP composites such as $\text{TiO}_2/\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ have been proposed to enhance the benzene oxidation under UV light or in the darkness [5]. Another composite, $\text{Ti}_{2-x}\text{N}_y\text{O}_2/\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$, was used to decompose gaseous acetaldehyde or nitrogen oxide acetaldehyde by a self-fluorescence assisted in the dark [6]. Another composite, $\text{Ag}_3\text{PO}_4/\text{Sr}_4\text{Al}_{14}\text{O}_{25}:(\text{Eu}, \text{Dy})$, decomposed the Rhodamine B without light assistance [7]. Here, the photocatalyst Ag_3PO_4 is excited by the light emitted from the LPP after turning off the UV excitation which was maintained during 30 minutes, this produced the degradation of rhodamine dissolved in an aqueous solution [7], then, and few studies about the photocatalytic properties of LPPs have been published.

The utilization of LPPs for photocatalytic applications has been attractive because the phosphorescent materials have electrons with high mobility from the valence band (VB) levels to the traps levels which can act as electrons storage and this fact can favor the photocatalytic properties [8]. These traps levels are usually generated by oxygen vacancy, defects, or impurities when the lattice is doped with Eu^{2+} and Dy^{3+} ions [8]. Based on the phosphorescence models, it is argued that electrons are stored in these traps states and, then, the energy can be slowly released to produce phosphorescence by electrons and holes recombination [9]. This slow release of electrons can allow larger amounts of electrons and holes (e-h^+) to be available for the production of hydroxyl radicals ($\text{OH}^\cdot$) which promotes the photocatalysis process [10]. The study of the photocatalytic properties of LPPs is important to find alternative photocatalysts other than TiO_2 which has been recently pointed out as a toxic for aquatic ecosystems [11]. Furthermore, several studies show that nanosized TiO_2 is toxic for many aquatic species like fish *Daphnia magna* and Rainbow fish [12]. Bioaccumulation into the gills of river fishes has also been reported [13]. Hence, micrometric sizes of the grains of the photocatalyst are suitable because they can be easily removed from water after their use. In addition, there are very few studies about Eu^{2+} , Dy^{3+} doped strontium/aluminosilicate powders and their utilization as photocatalysts. Thus, the aim of this work is to investigate the photocatalytic, structural, morphological, and optical properties of Eu^{2+} , Dy^{3+} doped-aluminate/aluminosilicate phosphors annealed at different temperatures in the range of 1000°C – 1300°C .

2. Experimental

2.1. Combustion Synthesis. $\text{Na}_2\text{O}_3\text{Si}_5\text{H}_2\text{O}$ (99.99%), $\text{Sr}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (99.9965%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.5%), $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%), $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%), NH_4NO_3 (99.9%), and H_3BO_3 (95%) reagents from Sigma Aldrich were dissolved in 25 mL of deionized water for approximately 45 minutes in a quartz beaker on a magnetic stirrer, and a transparent solution was formed. The Al/Sr ratio was 7.6 for all samples and was prepared using 0.01 moles of Eu^{2+} , 0.02 mole of Dy^{3+} , 1.5×10^{-3} mole of NH_4NO_3 , and 6.0×10^{-4} mole of H_3BO_3 . Also 0.01 mole of urea [$\text{CH}_4\text{N}_2\text{O}$] was added as fuel and it maximizes the combustion reaction. Next, the transparent blend was annealed at 600°C in atmospheric pressure and the exothermic reaction occurred (combustion process) during 10–40 seconds. As a result, (Eu,Dy)-doped strontium aluminate/aluminosilicates as-synthesized powders were obtained. Finally, the as-synthesized powders were put in alumina crucibles and annealed under reductive atmosphere during 4 h at four different temperatures: 1000°C , 1150°C , 1200°C , and 1300°C . After this, the blue-emitting LPPs of (Eu,Dy)-doped strontium aluminate/aluminosilicate powders were obtained.

2.2. Photocatalysis under UV and Solar Irradiations. For the photocatalysis experiments, the powders were first ground in an agate mortar until we got fine powders. The

photocatalytic degradation of the methylene blue (MB) was measured by monitoring the absorbance of MB dissolved in water at 665 nm. The photocatalytic process was carried out using a reactor fabricated with three 4 W UV lamps. Those lamps emitted UV light centered at 365 nm, with a FWHM around 12 nm. The samples for photocatalysis were prepared by mixing 30 mg of (Eu,Dy)-doped strontium aluminate/aluminosilicate powders with a solution 0.5 mM of MB in water. This solution was stirred in darkness during 1 h in order to adsorb the MB molecules on the surface of the powders. Afterwards, the UV lamps were turned on and samples of 1 mL were extracted every 30 minutes, the powders were separated from the liquid using centrifugation, and, then, the absorbance spectrum of the liquid was obtained by using a Cary-60 UV-Vis spectrophotometer in the range of 200 nm–700 nm. In the case of solar photocatalysis, the samples were exposed under sunlight during a sunny day from 10:00 am to 4:00 pm in Saltillo city, Mexico. The coordinates in this location were as follows: latitude, $25^\circ 25.706'$ North, longitude, $100^\circ 58.616'$ West, and height, 1581 m. The average solar irradiance was $\delta = 678 \pm 43 \text{ W/m}^2$ and it was measured with a photodiode 6450 Davis Solar Radiation Sensor.

2.3. Structural and Morphological Characterization. The X-ray diffraction (XRD) patterns of the (Eu,Dy)-doped strontium aluminate/aluminosilicate (1000 – 1300°C) were performed in a Bruker D-8 Advance diffractometer having the Bragg-Brentano configuration and CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$). The XRD patterns were measured in the range of $5^\circ \leq 2\theta \leq 80^\circ$ with 0.02° step size. Morphology of the samples was analyzed using a field emission electron JSM-7800F microscope and 200 kV of accelerating voltage.

2.4. Optical Characterization. Excitation spectra, photoluminescence spectra, and phosphorescence decay curves were obtained by using an Acton Research modular 2300 fluorometer. The fluorometer was coupled with a pair of SP-500i monochromators (Acton Research), a Xenon lamp (75 W) as excitation source of 75 W Xenon lamp, and a photo multiplier tube R955 (Hamamatsu). The chromaticity coordinates and the luminance of the samples were taken by using a Konica Minolta CS-2000 luminometer. For the measurements of phosphorescence, the (Eu,Dy)-doped strontium aluminate/aluminosilicate powders were irradiated during 5 minutes with a 365 nm UV lamp; then, the excitation was stopped and the phosphorescent signal as well as the luminance (L_v) was measured. The reflectance spectra of the powder samples were measured by utilizing Cary-5000 spectrophotometer coupled integrating sphere in the range of 200 nm–700 nm. All optical measurements were made at room temperature.

3. Results and Discussion

3.1. Structure and Morphology. Figure 1 show the XRD patterns of the (Eu,Dy)-doped strontium aluminate/aluminosilicate powders annealed in the range of 1000°C – 1300°C . The samples annealed at 1150°C , 1200°C , and 1300°C presented

TABLE 1: Summary of the luminance values, energy band- gap estimated values, CIE coordinate, and morphology of the samples annealed at different temperatures.

Sample	L_v (Cd/m ²)	Energy gap (eV)	CIE coordinates (x, y)	Morphology
1000°C	6	5.5	(0.2934, 0.3355)	Irregular micrograins
1150°C	27	5.8	(0.1708, 0.2209)	Bars, grains, and hexagons
1200°C	40	5.7	(0.1589, 0.1972)	Bars and hexagons
1300°C	15	5.8	(0.1637, 0.2048)	Hexagons

FIGURE 1: XRD patterns of the samples as function of temperature.

three crystalline phases: firstly, the SrAl_2O_4 hexagonal phase (JCPDS 311336), second the $\text{Sr}_3\text{Al}_{32}\text{O}_{51}$ hexagonal phase (JCPDS 440024), and lastly the NaSiAlO_4 orthorhombic phase (JCPDS 390376). The sample annealed at 1000°C had a fourth phase SiO_2 , and it is labeled with the symbol *. The SrAl_2O_4 and $\text{Sr}_3\text{Al}_{32}\text{O}_{51}$ standard patterns are plotted at the bottom of Figure 1 in black and gray vertical lines and the NaSiAlO_4 phase is marked with the θ symbol on the XRD patterns in all the samples. Furthermore, the intensity of the diffraction peaks of the NaSiAlO_4 phase is higher for the samples annealed at 1150°C and 1200°C in comparison with the samples annealed at 1000°C and 1300°C. This suggests that the amount of the NaSiAlO_4 is lower in the samples annealed at 1150°C and 1200°C.

The morphology of the calcined samples is illustrated in Figures 2(a)–2(d). The sample annealed at 1000°C shows clusters of coalesced grains in the range of 1–5 μm . Also, it can be observed that these irregular grains are porous, which can be beneficial for the adsorption of MB molecules on the surface of the powders. The samples annealed at 1150°C, 1200°C, and 1300°C also show irregular grains (see Figures 2(b)–2(d)) and the degree of coalescence among grains increased as the temperature increases. A zoom of the samples annealed at 1150°C and 1300°C samples is shown in Figures 2(e) and 2(f), respectively. The sample annealed at 1150°C (see Figure 2(e)) shows a morphology composed of bars (0.3–0.8 μm of average length), hexagons (0.2–0.5 μm of average diameter), and irregular grains (0.1–0.5 μm of average

size) and those ones are coalesced together to form bigger micrograins. In addition, the sample annealed at 1300°C consisted only in overlapped microhexagons with sizes in the range of 0.1–1.4 μm . Table 1 summarizes the morphologies found for each sample in this work.

3.2. Optical Properties. Figure 3 shows the diffuse reflectance spectra of samples with different annealing temperatures from 1000°C to 1300°C. The spectra show that the samples are highly reflective for wavelengths above 456 nm and they have a huge absorption band in the range of 225 nm–456 nm. The sample annealed at 1000°C showed the highest absorption of light in the visible range. The reflectance spectra show two main absorption bands: the first one is centered at 270 nm and it is attributed to the absorption of Eu^{2+} ions [8, 9]; the second absorption band located at 385 nm is attributed to $5d \rightarrow 4f$ allowed transition of Eu^{2+} [14]. The band-gap values of the samples were estimated by using the Kubelka-Munk function methodology [15, 16]. Figure 4 shows the Kubelka-Munk function for each sample; the values of band gap were obtained by intercepting the extrapolated linear part of the curves with the x-axis of the plot $(K-M)^{1/2}$ versus energy (eV). After this, the values of band-gaps obtained were in the range of 5.5–5.8 eV. Those high values suggest that our material behaves as an insulator.

Figure 5(a) depicts the excitation spectra of the samples annealed at different temperatures that were obtained by monitoring the emission at 455 nm. Those excitation spectra are broad bands centered at 363 nm and they are composed of three peaks at 270 nm, 355 nm, and 372 nm. The excitation peaks at 372 nm and 355 nm are related to Eu^{2+} excitation [9, 17] while the shoulder observed at 270 nm is associated with the well-known Eu-O charge transfer band [18]. Figure 5(b) shows the emission spectra of the samples annealed in the range of 1000°C–1300°C; it shows for all the samples an asymmetrical emission band centered at $\lambda_{\text{em}} = 455$ nm which is attributed to the $4f^6 5d^1 \rightarrow 4f^6 (^8S_{7/2})$ allowed transitions of the Eu^{2+} [3, 9, 19, 20]. This figure also shows on the left side images of the samples under UV and we can appreciate how the phosphorescent intensity increases as the temperature increases; however, the intensity decreased after we annealed the samples at 1300°C. This decrease of luminescence as a function of the temperature increase has been observed in $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ and it is attributed to higher degree of coalescence of particles, which, in turn, decreases the surface where the photoluminescence process can occur [21]. The asymmetrical band profiles shown in Figure 5(b) are related to the simultaneous presence of the

FIGURE 2: SEM images of samples annealed at (a) 1000°C, (b) 1150°C, (c) 1200°C, and (d) 1300°C. (e) and (f) are a zoom of the samples annealed at 1150°C and 1300°C, respectively.

FIGURE 3: Reflectance diffuse spectra of the samples annealed at different temperatures.

SrAl_2O_4 and $\text{Sr}_3\text{Al}_{32}\text{O}_{51}$ phases as observed in the XRD patterns. In both phases, the Eu^{2+} ions should be substituting the Sr^{2+} ions and, therefore, we observed a combined emission of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}/\text{Sr}_3\text{Al}_{32}\text{O}_{51}:\text{Eu}^{2+}$ which produced a broad blue-green emission band centered at 455 nm. If we have only

FIGURE 4: Plot of the Kubelka-Munk functions versus energy in eV for all samples annealed at different temperatures. The dashed lines are the tangent lines related to the procedure for the estimation of the band-gap energy; the intersection of the dashed lines with the horizontal axis gave us the values of the band-gap energy.

$\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ or $\text{Sr}_3\text{Al}_{32}\text{O}_{51}:\text{Eu}^{2+}$, we should observe a sharp emission band of Eu^{2+} centered at 516 nm ($\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$) or at 450 nm ($\text{Sr}_3\text{Al}_{32}\text{O}_{51}:\text{Eu}^{2+}$) [3, 19, 20] but those single

FIGURE 5: (a) Excitation spectra ($\lambda_{em} = 455$ nm) and (b) emission spectra ($\lambda_{exc} = 355$ nm) of the samples annealed at different temperatures.

FIGURE 6: Decay time curves of aluminate/aluminosilicate powders after excitation with UV light at 365 nm.

emissions were not observed in our case. Moreover, the NaSiAlO_4 phase does not contribute to the overall emission since it did not show yellow-orange emissions in the visible region under UV irradiation [22]. Further, it is worth noting that no emission of Eu^{3+} was observed, which suggests that our process of reduction is good enough to dope with only Eu^{2+} .

Figure 6 shows the phosphorescence decay curves of the samples annealed at different temperatures. Those ones were measured immediately after we stopped the excitation with UV light at 365 nm (we were exciting the samples during 5 minutes). As expected, the phosphorescence intensity of the sample annealed at 1200°C was the highest and it decreased by three orders of magnitude after 65 minutes, while the

rest of samples decreased their intensity by three orders of magnitude after only 10 minutes. This trend can be related to the fact that we have bars and hexagons at the same time in the sample annealed at 1200°C, since the other samples had grains or only hexagons and their intensity was lower. This means that bars can favor the phosphorescence but irregular grains can be detrimental for it. Furthermore, the mixture of morphologies can create intrinsic defects which enhances the phosphorescence intensity as reported in literature [23, 24]. We measured the luminance and CIE coordinates of our samples and the results are presented in Table 1; the sample annealed at 1200°C had the highest luminance (40 Cd/m^2) and its CIE coordinates were (0.1589, 0.1972); this last coordinate indicates that the color of phosphorescence is located in the blue-green region. Finally, the CIE coordinates of the rest of samples were similar even though the annealing temperature increased from 1000°C to 1300°C (see Table 1).

3.3. Photocatalytic Activity of Powders. Photocatalysis experiments were achieved by monitoring the percentage degradation of methylene blue (MB) in aqueous solution. Typically, the MB shows an absorbance band (A) at 665 nm and we measured the absorbance intensity of this peak as a function of time, since a decrease of intensity of this band indicates a decrement of the MB concentration (C). The following equation was used in order to calculate the MB degradation (%) as function of the time [25, 26]:

$$\text{Degradation (\%)} = \frac{A_0 - A_t}{A_0} \times 100, \quad (1)$$

where A_0 and A_t are the absorbance intensity values of the dye solution before and after irradiation, respectively. Figure 7(a) shows the percentage degradation of MB as a function of time. The degradation percentages of MB for

FIGURE 7: Degradation curves of MB: (a) under UV light at 365 nm and (b) under solar irradiation.

the samples annealed at 1000°C, 1150°C, 1200°C, and 1300°C after 360 min of UV excitation were 32%, 20%, 15%, and 38.5%, respectively. Thus, the samples annealed at 1000°C and 1300°C presented the highest percentage degradation and the lowest luminescent intensities. In contrast, the samples with the highest luminescent intensity (1150°C and 1200°C) exhibited the lowest photocatalytic activity. The decrease in the photocatalytic activity has been observed in other luminescent systems [25, 27] and this is due to the fact that the samples with lower luminescence generate more free-carriers (electron or holes) during the phosphorescence process compared with the samples with higher luminescence which use most of the electron/hole pairs to generate light emission. In consequence, as the availability of free-carriers is better, the photocatalytic activity is enhanced [28, 29]. Figure 7(b) shows the percentage degradation of the samples exposed to solar irradiation as a function of time. It is observed that the samples annealed at 1000°C, 1150°C, and 1200°C degraded 100% the MB dye after 300 min; this means an increase of 68%, 80%, and 85% of the MB degradation compared with the results obtained under UV light. The sample calcined at 1300°C degrades only ~88% of methylene blue in water solution after 360 min (see Figure 7(b)). This lower degradation percentage is related to the fact that higher annealing temperature promotes the coalescence of grains, which, in turn, reduces the surface area and this reduces the amount of methylene blue molecules adsorbed on the powders. This can be corroborated from SEM images, since we find bigger pieces of coalesced material in the samples annealed at 1300°C in comparison with the rest of samples (see Figures 2(a)–2(d)).

Based on the results mentioned above, we consider that our phosphors have modest photocatalysis activity (under UV light) compared to conventional TiO₂ nanoparticles [26,

28]. However, an advantage of our (Eu,Dy)-doped strontium aluminates/aluminosilicates as photocatalyst is the fact that they can be separated easily from water by using simple precipitation, which is more difficult for conventional TiO₂ nanoparticles. The best performance of our phosphors is presented under solar irradiation; this suggests that they can be used as photocatalysts in water treatment plans. We are currently working to obtain only one single phase, that is, only strontium aluminate or aluminosilicates in order to obtain the photocatalytic performance of each phase separately. Those results will be published in a subsequent article.

4. Conclusions

Strontium aluminate/aluminosilicate phosphorescent phosphors based on the mixture of SrAl₂O₄:Eu²⁺,Dy³⁺, Sr₃Al₃₂O₅₁:Eu²⁺,Dy³⁺, and NaSiAlO₄ were successfully fabricated by combustion synthesis and postannealed. The blue-green phosphorescence emission at 455 nm is ascribed to the 4f-5d allowed transition of the Eu²⁺. The sample with the longest phosphorescence was that annealed at 1200°C and it had a luminance of 40 Cd/m². The photocatalyst experiments with our samples demonstrated that these samples annealed at 1000°C and 1300°C showed the lowest luminescence intensity but the highest percentage degradation of MB under UV excitation at 365 nm (32% and 38.5%, resp.). When solar irradiation was used for the photocatalysis experiments, total degradation of MB was observed by using the samples annealed at 1000°C, 1150°C, and 1200°C after 300 minutes. Also those powders were separated easily from water by simple precipitation. Hence, the results suggest that our strontium aluminate/aluminosilicate phosphorescent blue phosphor powders can be useful for water cleaning systems.

Competing Interests

The authors declare that they have no competing interests.

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