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Title: Long lasting phosphors: SrAl₂O₄:Eu, Dy as the most studied material

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Abstract: The aim of this review is to present the progress in preparing phosphorescent particles based on the reported research. We highlight the recent progress on SrAl₂O₄: Eu, Dy particles by describing the advantages and disadvantages of the different synthesis methods. This long-lasting material combines several favorable attributes: is stable, efficient, and less toxic than their predecessors. For that, large attention has been paid to the development of an efficient preparation method of SrAl₂O₄ doped powders, including sol-gel method, hydrothermal synthesis, laser synthesis, combustion synthesis and solid state reaction. However, many of these techniques are not compatible with large-scale production and with the principles of sustainability. Industrial processing of highly crystalline powders usually requires high synthesis temperatures, typically between 1300 and 1900 °C, with long processing times, especially for solid state reaction. As a result, the average particle size is typically within the 20-100 μm range. This large particle size is limiting for current applications that demand sub-micron particles. The microstructure and size which are controlled through adjusting the experimental conditions have a great influence in the final photoluminescence response. Therefore, much effort has been devoted to exploring new strategies to obtain sub-micrometric particles, avoiding stringent, intricate, tedious, costly, or inefficient preparation steps and intrinsic toxicity or elemental scarcity. Moreover, persistent luminescent nanomaterials have attracted great interest to their potential application in solar cells, biological labeling and imaging and security encode. In addition, we describe the challenges and future of phosphorescent materials in regard to their synthesis, properties and applications. Finally, some further suggestions have been also addressed to enhance its photoluminescence response from the perspective of the synthesis. We believe that such a review can accelerate the developments of SrAl₂O₄-based materials.

Suggested Reviewers: Marcos Vinícius dos Santos Rezende Prof

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He possesses a large experience in rare earth doping in inorganic materials for optical applications.

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Current scientific work is primarily related to nanotechnology, high energy density materials, and novel alternative energy sources; developing synthetic routes to design nanoscale building blocks and using the bottom-up approach to explore new science and applications in diverse areas.

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His work has essentially concentrated on the processing of new crystalline phases for transparent ceramic and vitroc ceramic applications. He has a great background on Physicochemical and structural characterization of new polycrystalline materials. His research topics are: long-lasting luminescent glass ceramics and the development of cost-effective ceramic scintillators.

Opposed Reviewers:

Madrid, 18th May 2016

To the editorial board of *Renewable and Sustainable Energy Reviews*

Dear Editor,

We would like to submit the enclosed manuscript “*Long lasting phosphors: SrAl₂O₄:Eu, Dy as the most studied material.*” for consideration of publication as an article in *Renewable and Sustainable Energy Reviews*.

Several papers dealt with the synthesis of SrAl₂O₄:Eu²⁺, Dy³⁺ powders, which is a reflection of the recent research activities on this matrix. The development of SrAl₂O₄:Eu²⁺, Dy³⁺ powders are attractive because exhibit excellent phosphorescence properties and have a wide variety of applications. Increasingly, these materials in particular but also the phosphors are being investigated for applications requiring reduced particle dimensions. The traditional production process of nano-sized SrAl₂O₄:Eu²⁺, Dy³⁺ have many disadvantages such as high cost, complicated procedures and the obtained powders show a lower photoluminescence properties compared with micro-sized particles. Therefore, the phosphorescent particle production in the sub-micron range is currently a critical objective in industrial research.

In spite the above-explained importance of material, there is only one review¹ that covers partially the development of rare earth doped strontium aluminate materials, paying exclusive attention in optical properties.

This review gives a brief but interesting overview of the state of the art in the research on persistent phosphors, focusing on SrAl₂O₄:Eu²⁺, Dy³⁺, and offers, for the first time, a complete general outlook over 150 references in this topic, highlighting the applied preparations methods and their diverse morphologies as well as the optical properties and their use in the market. In addition, the current shortcomings and challenges on the further advancement of these extraordinary materials and possible solutions are discussed.

We have evaluated the synthesis routes employed to obtain highly crystalline SrAl₂O₄ sub-micron powders; the proper optimization of the synthesis process allows designing SrAl₂O₄:Eu²⁺, Dy³⁺ powders with great emission properties to technological applications. This issue can be considered a great challenge to scale-up the process for industrial uses.

Concerning the applications, these persistent luminescent materials for innovative power components are demanded strongly to develop sustainable materials, architectures and processes for power electronics suitable for use in energy technologies, contributing to the future of Smart Cities; bearing in mind that sub-micron particles based on SrAl₂O₄:Eu²⁺, Dy³⁺ are strong candidates for scintillation materials which are employed in contemporary radiation detectors for medical imaging, industrial inspection, dosimetry, and high-energy physics and can be used even in cosmetics.

Therefore, there is the necessity to define the limitations and further improvements to develop suitable materials for this wide range of applications.

We think that this review is perfectly suited for the audience of *Renewable and Sustainable Energy Reviews*. Moreover, taking into account the current interest on phosphorescent materials, particularly on sub-micron long-lasting afterglow particles, we are sure that this work will raise a high interest in the scientific community, and in this sense your journal will be the most suitable one, due to its broad audience.

All authors of this paper have read this work and confirmed its originality.

With my best regards,

Rocío E. Rojas Hernández

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(1) Kshatri, D. S.; Khare, a. Optical Properties of Rare Earth Doped Strontium Aluminate (SAO) Phosphors: A Review. *Opt. Spectrosc.* **2014**, *117* (5), 769–783.

1 **Abstract**
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4 The aim of this review is to present the progress in preparing phosphorescent particles based on the reported
5 research. We highlight the recent progress on SrAl₂O₄: Eu, Dy particles by describing the advantages and
6 disadvantages of the different synthesis methods. This long-lasting material combines several favorable
7 attributes: is stable, efficient, and less toxic than their predecessors. For that, large attention has been paid to the
8 development of an efficient preparation method of SrAl₂O₄ doped powders, including sol-gel method,
9 hydrothermal synthesis, laser synthesis, combustion synthesis and solid state reaction. However, many of these
10 techniques are not compatible with large-scale production and with the principles of sustainability. Industrial
11 processing of highly crystalline powders usually requires high synthesis temperatures, typically between 1300
12 and 1900 °C, with long processing times, especially for solid state reaction. As a result, the average particle size is
13 typically within the 20-100 μm range. This large particle size is limiting for current applications that demand
14 sub-micron particles. The microstructure and size which are controlled through adjusting the experimental
15 conditions have a great influence in the final photoluminescence response. Therefore, much effort has been
16 devoted to exploring new strategies to obtain sub-micrometric particles, avoiding stringent, intricate, tedious,
17 costly, or inefficient preparation steps and intrinsic toxicity or elemental scarcity. Moreover, persistent
18 luminescent nanomaterials have attracted great interest to their potential application in solar cells, biological
19 labeling and imaging and security encode. In addition, we describe the challenges and future of phosphorescent
20 materials in regard to their synthesis, properties and applications. Finally, some further suggestions have been
21 also addressed to enhance its photoluminescence response from the perspective of the synthesis. We believe that
22 such a review can accelerate the developments of SrAl₂O₄-based materials.
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28 *KEYWORDS:* phosphorescent material; afterglow; persistent luminescence; sub-micron size; SrAl₂O₄
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1. Introduction.

Luminescent materials, also called phosphors, emit light after absorption of energy from an excitation source. These materials can classify by different ways such as their chemical family, application or even by the excitation source. According to the excitation, they can be categorized as photoluminescent, cathodoluminescent, X-ray luminescent, triboluminescent, sonoluminescent, electroluminescent, thermoluminescent, chemiluminescent and bioluminescent.

Up to now, a huge number of luminescent materials have been developed for different applications, highlighting fluorescent proteins¹, organic pigments¹, metal complex^{2,3}, semiconductors⁴ and inorganic phosphors^{5,6}. In spite of the advances achieved, the improvement of their optical features is still a challenge. Luminescent materials are mostly inorganic materials. Nevertheless, lately organic luminescent materials have acquired notable interest. Here, we are going to focus on inorganic phosphors.

The following article will review some preparation methods of inorganic phosphors focusing the attention on the advanced synthesis processes of Strontium monoaluminate (SrAl_2O_4) based materials, and emphasizing on the relationships between structure and photoluminescence response. In the first part, we give a general introduction to the background and characterization methods of inorganic luminescent materials for elucidating the luminescence mechanism different. In the second part, we focus on the design and synthesis of SrAl_2O_4 -based materials; covering from classical synthesis methods to advanced synthesis methods such as hydrothermal, co-precipitation, microemulsion, sol-gel method and combustion methods. We place special emphasis on in the development of new strategies to obtain sub-micrometric particles, avoiding stringent, intricate, tedious, costly, or inefficient preparation steps and intrinsic toxicity or elemental scarcity. It is worth noting that we reported a large photoluminescence response on SrAl_2O_4 -based materials with sub-micrometric size particle obtained by an innovate process based on molten salt synthesis. In the third part, we illuminate the relationships between synthesis routes and photoluminescence activity, discuss some existing challenges, suggest possible methods for further improving photoluminescence, and provide some conclusions. Finally, we paid special attention on their applications in the field of luminous markers

2. Basic Concepts

Inorganic Luminescent Materials

Inorganic phosphors can be also classified depend on the persistence of the luminescence; being fluorescent if emission of light remains 10^{-9} - 10^{-7} s after the excitation and phosphorescent when the life time is higher⁷.

In relation to luminescence mechanism, the emission can be generated by an optical center (luminescence center), charge transfer or from optical transitions between host lattice related band states. In luminescence center, the optical transition can involve electronic states of the ion only, so the emission spectrum shows sharp bands. If electronic states participate in chemical bonding several parameters play an important role as: the nature of the bonding, the charge and distance of adjacent ions and crystalline symmetry. The electronic transition can be: intraconfigurational $d \rightarrow d$ (Mn^{2+} , Cr^{3+}) or $4f \rightarrow 4f$ (Eu^{3+}) or interconfigurational ($4f \rightarrow 5d$ transitions, Eu^{2+} , Ce^{3+}). Intraconfigurational transitions are spin forbidden by selection rule but they are partial allowed by the electric dipolar character resulting. On the contrary, interconfigurational transitions are allowed, and usually they show broad emission band. In the charge transfer mechanism, the optical transition takes places between different kind of orbitals or electronic states or different ions⁷⁻⁹.

Persistent luminescence

Persistent luminescence (phosphorescence) is a phenomenon through which light emission persists for a long time after the irradiation had finished. Likely, the first material that exhibits this phenomenon was the so-called Bologna stone, which emits light due to some natural impurities. During the last decades several persistent phosphors are widely developed to get phosphors that cover all the visible emission spectrum. The experimental material research has allowed the development of about a hundred of persistent luminescent materials with the challenge to obtain a sufficiently strong and long lasting luminescence.

The life time, phosphorescence decay time or afterglow time is defined as the time that the human eye detects emission of light when the excitation has finished. The visibility threshold or the limit light perception of dark-adapted human eyes is 0.32 mCd/m^2 (100 times the light perception of the scotopic vision)¹⁰.

Different regulations have been employed to evaluate the photoluminescence of commercial products. However, the most used is the German norm "DIN 67510-1: Photoluminescent pigments and products-Part 1:

1 Measurement and marking at the producer"¹¹. This regulation establishes the luminance at the following
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3 intervals after the exposure lamp is switched off: 10, 60 and 520 minutes. In each case the samples are irradiated
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5 10 minutes by a Xe Arc Lamp (1000 lux).
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8 Generally speaking, there is not a standardized way of measuring and defining persistent phosphors
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10 properties. Nonetheless, the majority of decay curves are taken when the sample is irradiated with
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12 monochromatic light at 350, 365 and 375 nm during 5 and 10 minutes ¹²⁻¹⁹ and by a solar simulator in a lesser
13
14 extent²⁰.
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17 **3. Persistent luminescence materials**

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19 Persistent luminescence materials frequently consist of an inorganic matrix (known as host) and activated
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21 doping ions (activator). Generally, the doping ion is a rare earth element (Ln^{3+} : Eu^{3+} , Eu^{2+} , Ce^{3+} , Tb^{3+} , Sm^{3+} , Pr^{3+} ,
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23 Dy^{3+} , Er^{3+} , Tm^{3+} , Nd^{3+}), but it can be also a transition metal such as V^{3+} , Cu^{2+} , Mn^{2+} , Ti^{4+} , Sn^{2+} , Co^{2+} , Bi^{3+} or Pb^{2+} .
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25 This active center can act as emitter or trap: the role of the emitter is giving radiation after the excitation and the
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27 trap stores the excitation energy. However, there still exists strong disagreement on the exact trapping
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29 mechanism for the most studied type of persistent luminescent materials.
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33 **Figure 1.** provides an overview of the compounds that exhibit persistent luminescence. This chart has been
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35 made taking in account the main compounds taken from the literature ^{5,21-45}. The vertical axis collects different
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37 host and the horizontal symbolize the electromagnetic spectrum in the visible range. Inside the chart, there are
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39 data points related to the chemical elements that dopes the matrix (host) with their label. The host can be doped
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41 by one or more cations. The emission color can be modulated as a function of the dopant and the host material.
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43 For example Zinc sulfide (ZnS) emits blue light ($\lambda=452\text{nm}$) upon excitation when the host is doped with Eu^{3+} and
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45 exhibit green ($\lambda=510\text{nm}$) and yellow ($\lambda=570\text{nm}$) emission if it is doped with Cu^+ or/and Co^{2+} and Mn^{2+} and Ce^{2+} ,
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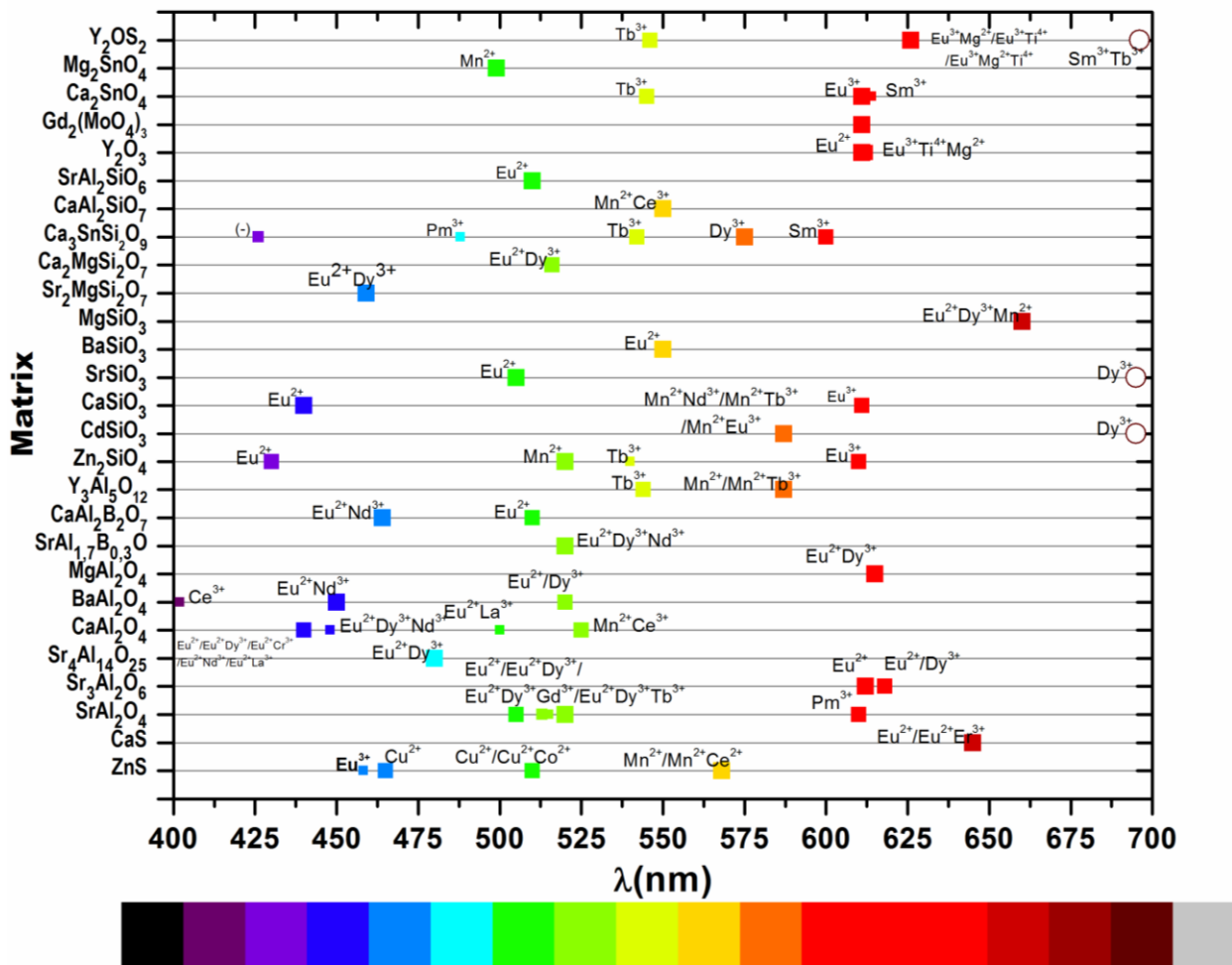


Figure 1. Overview of the compounds that exhibit persistent luminescence: The vertical axis collects different matrix and the horizontal axis symbolize the electromagnetic spectrum in the visible range. Inside the chart, there are data points related to the chemical elements that dopes the matrix (host) with their label.

The sulfides are known mainly for their fluorescence properties, but nonetheless they are phosphorescent through a suitable well synthesis and doped. These compounds have attracted great interest because of its electroluminescent properties for Light-Emitting Diodes (LEDs). ZnS doped with copper (Cu) and cobalt (Co)²¹ has been the most attractive for persistent luminescence and they have been used in luminous clocks, paints and children's toys. However, their persistent luminescence is short; to solve this issue, radioactive elements such as Tritium (³H) and Promethium (¹⁴⁷Pm) were incorporated, achieving a long persistent luminescence time. Their consumption growth but over time the restriction in the use of radioactive elements implied the reduction of their use. Therefore, the lack of suitable phosphorescent materials encourages the research in this field.

In relation to calcium sulfides (CaS), they are doped with Eu²⁺, Tm³⁺ and Ce⁺ or with Bi³⁺ emitting red and blue light, respectively^{24,25}. The strontium sulfide matrix (SrS) doped with Eu²⁺ and Dy³⁺ shows red emission²⁶.

1 This characteristic emission has had significance in LED industry. However, sulfides are hygroscopic and have
2
3 low stability, being unpromising in phosphorescent material field.
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6 The discovery of the long-lasting afterglow properties of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ by *Matsuzawa et al*⁴⁶. put the use of
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8 $\text{ZnS}:\text{Co}$, Cu aside due to the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ brightness that is ten times than $\text{ZnS}:\text{Co}$, Cu . These values
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10 encouraged the research in strontium aluminates and another's aluminates.
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13 **Figure 2.** shows the lifetime of the different compounds gathered in **Fig.1** the afterglow times ranging from
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15 several minutes to several hours after excitation mostly by ultraviolet light.
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18 Rare earth-doped alkaline earth aluminates MAl_2O_4 ($\text{M}=\text{Ca},\text{Sr},\text{Ba}$) family has been the most extensively
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20 studied. Calcium aluminate doped with Eu^{2+} , Dy^{3+} and Nd^{3+} and B^{3+} emits in the blue region²⁸⁻³⁰, while doped
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22 with Mn^{2+} and Ce^{3+} the emission shifts to the green region³³. The lifetime of these compounds is ca. 6 hours.
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25 Concerning barium aluminates, the lifetime estimated is ca. 7 and 1 hour for Eu^{2+} and Nd^{2+} ³¹ doped and Eu^{2+} ,
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27 Dy^{3+47} , respectively.
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30 Particularly, $\text{SrO}-\text{Al}_2\text{O}_3$ system has been mainly researched due to their longest afterglow times; specially
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32 focusing on $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ ⁴⁸⁻⁵², SrAl_4O_7 ⁵³, SrAl_2O_4 ^{20,54-58} and $\text{Sr}_2\text{Al}_3\text{O}_6$ ^{34,35,59} doped with Eu^{2+} and Dy^{3+} , whose emission
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34 bands are centered in blue ($\text{Sr}_4\text{Al}_{14}\text{O}_{25}$), green (SrAl_4O_7 , SrAl_2O_4), and red ($\text{Sr}_2\text{Al}_3\text{O}_6$).
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37 Silicates show also some interesting properties and can be classified in two families: MSiO_3 ($\text{M}=\text{Ca}, \text{Ba}, \text{Sr}, \text{Cd}$,
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39 Mg)^{28,60} and $\text{M}_2\text{MgSi}_2\text{O}_7$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$)^{38,41,43}. Being the longest afterglow time (>10h) observed in $\text{Sr}_2\text{MgSi}_2\text{O}_7$
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41 doped with Eu^{2+} and Dy^{3+} ⁶¹.
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44 Regarding oxides, the lifetime is ca. 1 hour for CaO , SrO and BaO doped with Eu^{2+} ⁶ and for Y_2O_3 doped with
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46 Eu^{3+} or co-doped with Mg^{2+} and Ti^{4+} ; emitting in the red region³².
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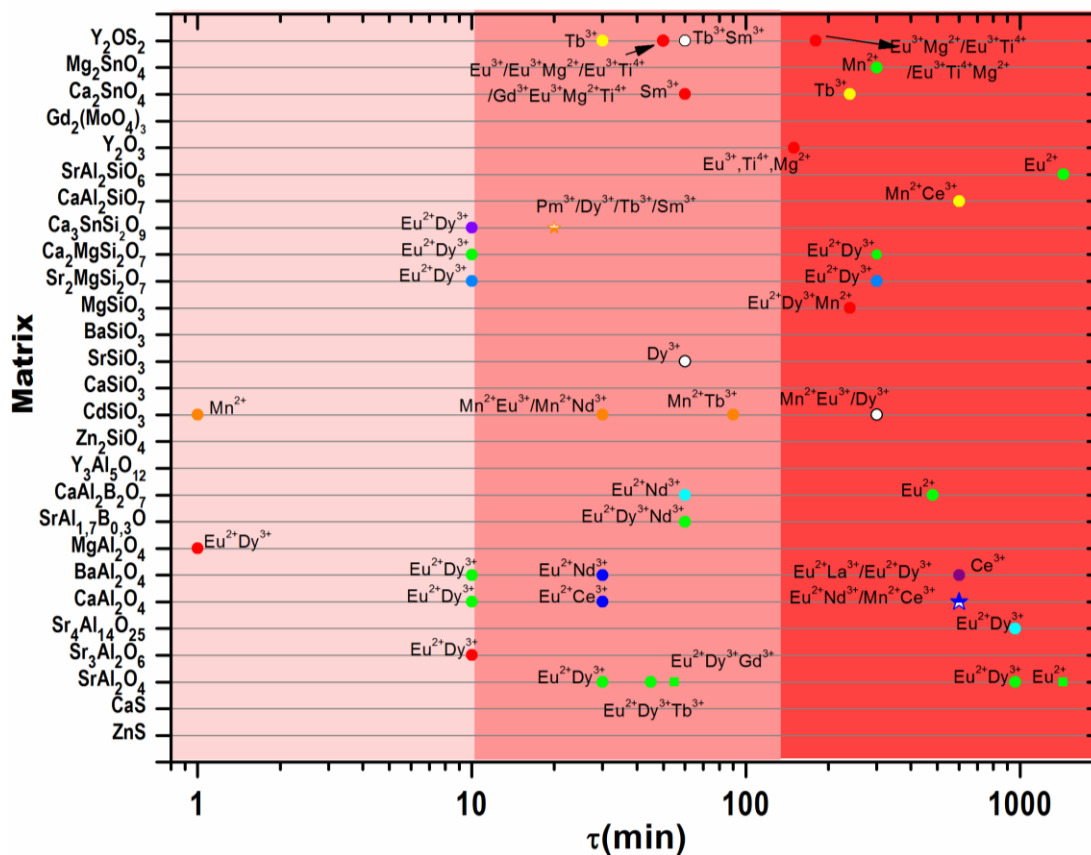


Figure 2. Overview of the lifetime of the different compounds that exhibit persistent luminescence: The vertical axis collects different matrix and the horizontal axis shows the afterglow times ranging from minutes to several hours after excitation was stopped mostly by ultraviolet light. Inside the chart, there are data points related to the chemical elements that dope the matrix (host) with their label.

There is enormous number of persistent luminescent materials, but nonetheless strontium aluminates are the most interesting host due to their properties such as bright, lifetime (>16h, threshold value: 0.32 mcd/m²) and stability. This means, the use of these compounds in large variety of applications. However, the well-known drawback is the weak water resistance, breaking bond of O-Sr-O, so this phosphor tends to hydrolyze and deteriorate. For this reason, some encapsulation techniques have been carried out by means of inorganic or organic layers. These layers have not had the result expected to prevent hydrolysis of strontium aluminate, moreover the water resistance improve at expense of a loss of luminescence intensity.

Regarding the persistent luminescence mechanisms, basic and complex mechanisms have been suggested. However, there still exists strong disagreement on the exact trapping mechanism for the most studied type of persistent phosphors. Many effects and details are not fully understood, but the research in this field has a

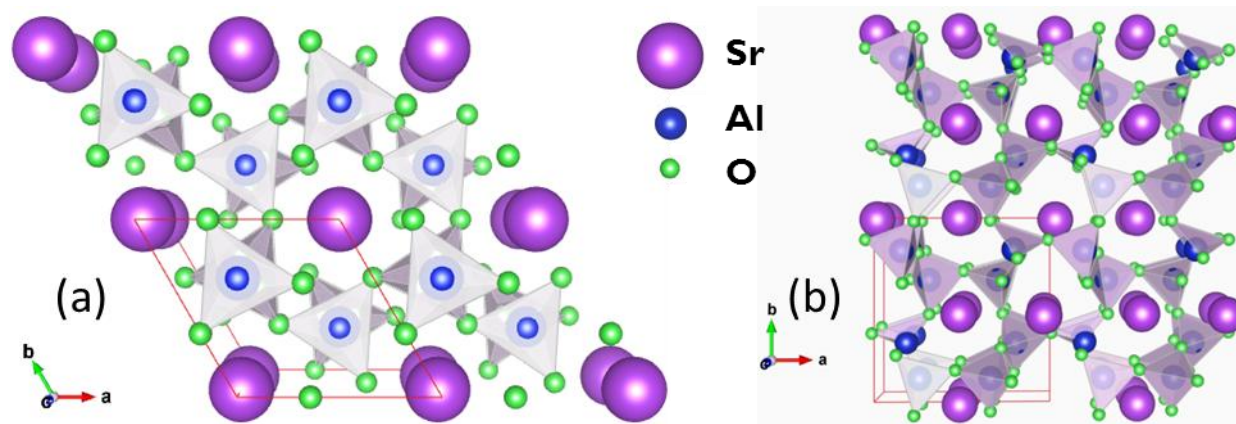
1 promising future taking in account the development of experiments with techniques as XANES, EXAFS and
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3 EPR, which can provide useful information.
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6 **4. Strontium monoaluminate, SrAl₂O₄**

8 *Structural description*

10 Strontium aluminate, SrAl₂O₄ host, has stuffed tridymite type structure, even though the crystal structure is
11 related to AB₂O₄ spinel structure. This behavior can be explained due to the large size of Sr²⁺(1.18 Å), avoiding
12 the spinel structure formation⁶².
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17 The structure consist of tetrahedral [AlO₄]⁵⁻ layers that share vertex forming six-member rings. Strontium
18 cations, Sr²⁺, are found within the hexagonal cavities formed by AlO₄ tetrahedra. Sr²⁺ cations can occupy two
19 nonequivalent sites (with nine adjacent oxygen ions) with coordination 7 or 7+2⁶³. **Figure 3.** shows the schematic
20 representations of the SrAl₂O₄ polymorph.
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43 **Figure 3.** Schematic representations of the SrAl₂O₄ polymorph: (a) Hexagonal SrAl₂O₄ polymorph. (b) Monoclinic SrAl₂O₄
44 polymorph obtained by VESTA⁶⁴.
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48 Strontium aluminate, SrAl₂O₄, has two crystallographic polymorphs: monoclinic symmetry that it is stable at
49 temperatures below 650°C and hexagonal symmetry (ideal undistorted structure) that it is stable above this
50 temperature. Monoclinic symmetry with space group P2₁ (a=8.447 Å, b=8.816 Å, c=5.163 Å, β=93,42) and
51 hexagonal symmetry with space group P6₃22 (a=5.140 Å, c=8.462 Å). Some authors establish that the monoclinic
52 phase, P2₁, transforms directly into the hexagonal phase, P6₃22 and it is a reversible process⁶⁵. However, Avdee
53 *et al.*⁶⁶ studied in detail the structural behavior to solve inconsistency in the results reported. They suggested a
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1 monoclinic \leftrightarrow hexagonal phase transition at 680°C, being the space group $P6_3$ and a second-order transition to
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3 $P6_322$ at 860°C.
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5 By Raman spectroscopy, there is not an accurate study about tridymite structure due to its complexity. The
6 theory group predicts 81 active modes for monoclinic phase, $P2_1$, and 20 and 61 for hexagonal phase, $P6_322$ and
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8 $P6_3$, respectively. $SrAl_2O_4$ structure is formed by AlO_4 units, so Raman modes can describe the internal vibration
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10 of AlO_4 , rotational vibration of this units and translational modes due to the Sr^{2+} cations located in polyhedral
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12 cavities. Raman modes are assigned to tetrahedral tilts for Raman shift below 150 cm^{-1} , to stretching vibration
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14 for Raman shift above 600 cm^{-1} and the most intense Raman mode at 465 cm^{-1} to bending vibration of O-Al-O
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16 angle^{56,65}.
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20 ***SrAl₂O₄ doped with rare earths***

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23 After the discovery in 1996 of $SrAl_2O_4: Eu^{2+}Dy^{3+}$ as new persistent luminescent compound by *Matsuzawa et al.*⁴⁶,
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25 $SrAl_2O_4$ host has been doped mainly with europium and co-doped with dysprosium to obtain a persistent
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27 material, there are few works that includes other dopants such as Ce^{3+} ⁶⁷, $Eu^{2+} Dy^{3+} Gd^{3+}$ ⁶⁸, $Eu^{2+} Nd^{3+}$
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29 ⁶⁹, $Eu^{3+}Ho^{3+}$ ⁷⁰ and $Dy^{3+}Yb^{3+}$ ⁷¹. Concerning the luminescence response of $SrAl_2O_4$ doped with Eu^{2+} and Dy^{3+} ,
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31 some authors reported that only the monoclinic structure exhibits luminescent properties^{15,56}. However, *Jia et al.*⁷²
32
33 suggested that the hexagonal $SrAl_2O_4$ polymorph has higher emission efficiency than the monoclinic polymorph.
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37 ***Synthesis methods***

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40 The synthesis method for $SrAl_2O_4$ -based phosphorescent materials plays a significant role in determining the
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42 features of particle and crystal size, afterglow properties, fluorescent quantum efficiency and the defects. .
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44 Generally speaking, the powders based on $SrAl_2O_4$ consist mostly of micrometer-sized particles and crystals;
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46 being the average particle size typically within the 20-100 μm range and the crystallite size higher than 15 nm
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48 ^{73,74}. This large particle size is limiting applications that demand sub-micron particles. For this reason and due to
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50 quantum confinement effect which leads to novel optoelectronic properties, nanosized luminescent particles are
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52 under extensively study. Emission, lifetime and luminescence quantum efficiency depend strongly on both the
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54 particle size range and on the microstructure. The main disadvantages of nanosized phosphors are the
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56 increasing number of defects due to the synthesis conditions and the larger surface to volume ratio that decrease
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58 the quantum efficiency by radiationless transitions. However, the crystal size has also a great influence on the
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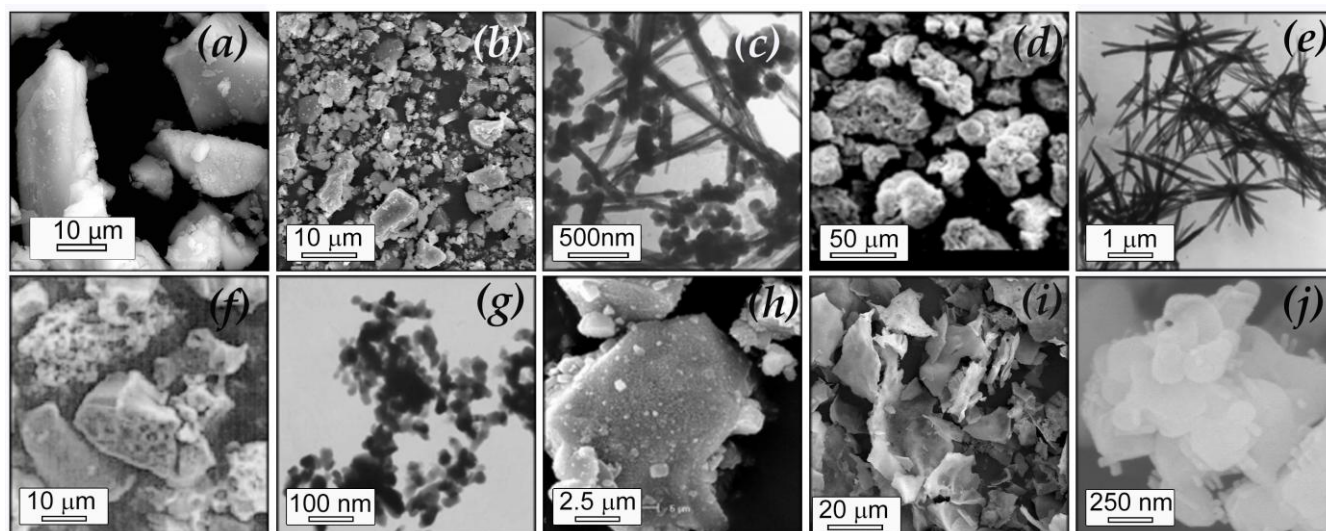
1 photoluminescence properties. For example, the absorption of excitation light is decreased by the strong light
2 scattering of nanocrystals, and therefore, the reduction of the intensity emission. Despite the fact that the
3 nanosized luminescent material presents many advantages over the bulk samples, their synthesis is still a
4 challenge.
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10 Intensive scientific research has been focused on the synthesis methods of $\text{Eu}^{2+}/\text{Dy}^{3+}$ doped strontium
11 aluminate phosphor due its green emission band. The conventional solid state method^{16,46,75} is widely accepted
12 for the synthesis of phosphor materials for commercial application as compared to other methods such as sol-gel
13 method^{76,77}, hydrothermal synthesis¹⁴, laser synthesis⁷⁸ and combustion synthesis^{29,79-81} due its good brightness
14 and higher luminescence intensity as compared to the other methods. However, for a large scale production
15 solid state reaction requires high temperatures $> 1300^\circ\text{C}$ during long-time ($>10\text{h}$), which result in a waste of
16 energy. Also the composition and the morphology are inhomogeneous. And as we said earlier, the average
17 particle size is some tens of microns. **Figure 4(a)** shows the microstructure of the powders obtained by solid state
18 reaction. In effect, the particles ranging from 8 to 40 μm have an irregular shape with sharp fracture surfaces⁸².
19 This latter aspect is derived from followed grinding process, so a higher primary particle size is assumed. To
20 reduce particle size an intensive grinding as ball milling is required. By wet-milling different approaches have
21 been carried out: (i) employing ethanol absolute as a milling medium and by attrition process, it is possible to
22 decrease the particle size until 4 μm , with a drastic decreasing of the luminescence response⁸². (ii) employing
23 ethyl acetate as a milling medium during 9 days, powders with few particles greater than 10 μm are obtained
24 and retained the photoluminescence properties⁸³. In addition, dry-milling approach have been developed: (i) by
25 high-energy dry milling, it is possible to reduce the particle size, but an agglomeration state is generated and (ii)
26 by low-energy dry milling, powders with an average particle size ca. 3 μm have been obtained (**Fig. 4(b)**).
27 However, in all the procedures carried out, the luminescence response decreases due to the defects created at the
28 particle surface during the milling step and the crystallite size reduction⁸⁴. In recent years, there has been
29 increasing interest in the use of persistent luminescence materials with sub-micrometer particles size for
30 emergent applications such as imaging and security encode.
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57 In contrast, soft chemical methods (hydrothermal, co-precipitation, microemulsion and sol-gel method) and
58 combustion and microwave synthesis have the advantage of controlling morphologies and sizes but these need
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several number of synthetic steps and the persistent luminescence is significantly reduced in comparison with the micrometer powder^{29,65,79,80,85-87}. Initially, the thermal treatments are generally low (<350°C), nevertheless post- thermal treatments usually are carried out to improve the crystallinity of the powders. As a consequence the particle size grows.

By sol-gel synthesis, the process can be carried out from colloidal solutions or from alkoxides; obtaining a structure more dispersed or agglomerated; employing an organic or polymeric solvent during the hydrolysis step. The gel is first heated at 100°C for 10 to 24 hours, after that the resulted precursor gel powder is heated for some hours (2 to 16) in a reductive atmosphere (active carbon or N₂-H₂ atmosphere) at 1100-1400°C by usual solid state reaction technique. E. Cordoncillo *et al.*⁷⁷ modified the process by the addition of B₂O₃ to reduce the processing temperature; obtaining the monoclinic polymorph at 1200°C. Although the thermal treatment is reduced and the particles are more dispersed and have a homogeneous size, the final photoluminescence response is strongly less than the particles obtained by solid state route^{56,65,88}. The annealing process has also been carried out by a double treatment to improve the persistent of the luminescence. However, the life time of the submicrometer particles (ca. 90 nm) is only 10 minutes and the intensity has been reduced to about one order of magnitude⁸⁹. Tang *et al.*⁷⁶ obtained powders at 900°C with an average particle size ca. 60nm, **Fig. 4(c)** and an afterglow time of 14 hours considering the 0.32mcd/m² photopic threshold level. The main disadvantages of sol-gel process are large volume of solvent required and the complex, moreover the process need post annealing treatments.



1 **Figure 4.** FE-SEM micrographs of as received (a) commercial SrAl₂O₄: Eu, Dy particles with sizes of 8-40 μm and (b) after low-
2 energy dry milling during 40 min. FE-SEM micrographs SrAl₂O₄: Eu, Dy particles synthesized by (c) sol-gel, (d)
3 microemulsion, (e) hydrothermal, (f) microwave and (g-h) combustion synthesis. Reprinted with the permission from
4 references ^{76, 90, 14, 74, 73} and ²⁵ respectively. (i) Flaky particles 5–25 μm in size obtained by combustion synthesis. (j) Powder
5 synthesized by molten salt. Reprinted with the permission from ref ^{80,84,91}, respectively.
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10 The synthesis of luminescent nanopowders demands the control of the particle size and its distribution. For
11 this reason, microemulsion-assisted synthesis is employed. Basically this route has been used to synthesize
12 metals, metal oxides and ceramic and sulfur compounds. Concerning nanophosphors, the crystallinity has been
13 improved and the annealing temperature has been reduced in systems as Y₃Al₅O₁₂:Eu³⁺³⁶ and BaMgAl₁₀O₁₇:Eu²⁺
14 ⁹² synthesized by microemulsion. For the preparation of strontium aluminates, Sr₄Al₁₄O₂₅: Eu, Dy⁴⁹ particles with
15 an average size ≈ 50-200 nm has been obtained. SrAl₂O₄: Eu, Dy powders were prepared via an ordinary⁹⁰ and
16 reverse microemulsion⁹³ process as well. By usual process, it is necessary to carry out an annealing process in
17 reducing atmosphere and by a double- thermal treatment at 1000 and 1100°C, where the particles obtained grow
18 significantly, ca. 3 -50μm, **Fig. 4(d)**. Via a reverse microemulsion technique particles with an average particle size
19 ca. 40 nm were obtained at 900°C with controlled morphology. However, the photoluminescence response has
20 no comparative study that limits its evaluation ⁵⁸.
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35 Hydrothermal route, as well as sol-gel and microemulsion approaches enhance the particle size control and
36 morphology. Needle-like SrAl₂O₄: Eu, Dy powders with a particle size ca. 1 μm were obtained via a
37 hydrothermal process with a further thermal treatment at 1200°C ¹⁴ **Fig. 4(e)**. Regarding the photoluminescence
38 intensity and decay time, the phosphors revealed long-lasting properties, but the results are not comparable with
39 particles synthesized by other routes.
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47 In order to reduce the complexity in processing, short and low thermal treatments without post annealing
48 treatments techniques such as combustion, laser and microwave synthesis methods have also been employed. J.
49 Geng *et al.*⁷⁴ synthesized SrAl₂O₄: Eu, Dy powders by a microwave route. **Fig. 4(f)**; The reaction took only 15 min
50 but the powders have a large size (ca. 4.8 μm) and the initial luminescent intensity of the decay curve decreases
51 greatly compared with powders obtained by solid state reaction.
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1 By laser synthesis, the powders can obtain in a single step. However the phosphorescent material has a grain
2 size over 10 μm ⁷⁸. In addition the decay curves showed that the persistence of luminescence last only for 3
4 minutes.
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8 Combustion technique appears to be a promising route for the preparation of inorganic powders. This route is
9 versatile and rapid, and requires relatively low temperatures, 600°C. It allows uniform doping in a single step
10 and a reductive atmosphere is not necessary ^{86,94}. Combustion synthesis consisted of exothermic reaction in a
11 homogeneous solution of oxidants in the presence of fuel. A number of suitable fuels are available, notably
12 glycine, but citric acid, carbohydrazide or urea are also used to initiate the decomposition reaction. The particles
13 based on SrAl_2O_4 : Eu, Dy obtained by usual combustion method are in the nanometer^{81,95}, **Fig. 4(g)**, and in
14 micrometer range²⁵, **Fig. 4(h)**; However, particles are largely agglomerated, but nonetheless are less dense and
15 more highly sintered than those obtained by alternative methods. It is important to remark the relatively low
16 density of the thin flakes particles that could avoid a high energy ball milling process, for further particle size
17 reduction almost obligatory in solid state reaction.
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30 An optimization of the combustion synthesis by adding an oxidizing agent as nitric acid allowed to
31 incorporate a major quantity of urea in order to avoid post thermal treatments, and thus the photoluminescence
32 response improves for nanostructured thin flakes with $\leq 1\mu\text{m}$ in thickness ⁷⁹, **Fig. 4(i)**. Moreover, by a dry
33 grinding process it is possible to reduce the particle size; achieving sub-micron size nanostructured particles
34 which can be used in applications requiring small particle size and high phosphorescence⁸⁰. Qiu et al.⁹⁶, on the
35 other hand, processed in one step nano particles, 100nm, with an afterglow time around 7 hours (threshold
36 intensity: 0.32 mCd/m²).
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46 Recently, SrAl_2O_4 : Eu, Dy has been successfully synthesized by molten salt method using the (NaCl-KCl)e
47 eutectic mixture as molten flux⁹¹. The use of this innovative process induces an increase in the reaction rate and a
48 reduction of the formation temperature of SrAl_2O_4 in comparison with the classic solid-state method. As a
49 consequence, the formation of SrAl_2O_4 is favored at low temperatures; synthesizing submicrometer
50 phosphorescent particles at 900 °C for 1 h, **Fig. 4(j)**. The molten salt process possesses relevant advantages over
51 the previous methods for the synthesis of strontium aluminates. Due to the reduction of multistep in the
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processing, the main improvement is that synthesis in flux enlarges crystallinity and therefore large luminescent response; avoiding a multistep process.

Table 1. Lifetime and particle size of the powders based on SrAl_2O_4 : Eu, Dy prepared by different synthesis methods. The thermal treatments are detailed in the table. The lifetime corresponds with an Intensity: 0.32mCd/m, with the exception of values marked with * that have been collected in arbitrary units.

Dopant	Co-dopant	Synthesis Route	Thermal treatment	Lifetime (min)	Particle size	Ref
Eu ²⁺		Solid State	1400°C 2-4 h	1440	-	16
Eu ²⁺	Dy ³⁺	Solid State	1400°C 6 h	1000*	10 μm	75
Eu ²⁺	Dy ³⁺	Solid State	-	100	20-30 μm	46
Eu ²⁺	Dy ³⁺	Sol-gel	90°C + Post-T.T. 1200°C	100	-	56
Eu ²⁺	Dy ³⁺	Sol-gel	100°C + Post-T.T. 900°C 16h	840	60nm	89
Eu ²⁺	Dy ³⁺	Sol-gel	60°C + Post-T.T. 600+1000°C	10	-	76
Eu ²⁺	Dy ³⁺	Hydrothermal	1200°C	5*	1 μm	14
Eu ²⁺	Dy ³⁺	Microemulsion	Post-T.T. 1000+1100°C	-	3-50 μm	90
Eu ²⁺	Dy ³⁺	Microwave	15 min 600W	12*	-	74
Eu ²⁺	Dy ³⁺	Laser	-	3*	-	78
Eu ²⁺	Dy ³⁺	Combustion	500°C + Post-T.T. 1000°C	120*	15-30 nm	95
Eu ²⁺	Dy ³⁺	Combustion	600°C	420	100 nm	29
Eu ²⁺	Dy ³⁺	Combustion	500°C + Post-T.T. 1100°C	-	15-45 nm	97
Eu ²⁺	Dy ³⁺	Combustion	600°C	10*	Flakes: Lenght ≈10 μm, thickness ≤1 μm	79
Eu ²⁺	Dy ³⁺	Combustion	600°C + Post-T.T. 900°C 1h	-	≤0.5 μm	80
Eu ²⁺	Dy ³⁺	Spray Pirolisis	1400°C	-	10-250 nm	98
Eu ²⁺	Dy ²⁺	Molten salt	900°C 1h	60	≤0.5 μm	91

Commercial phosphorescent materials

The production of nano phosphorescent powders is still in its early stages. Although, the available literature provides several routes to synthesize nanopowders, the commercial phosphorescent material based on SrAl_2O_4 : Eu, Dy are micrometric particles produced by solid state reaction till now. Only the materials synthesized by conventional way at high temperatures exhibit properties that are sufficient for technological application. A

1 patent study related to long-lasting phosphors shows that the majority of patents in this topic are associated to
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3 aluminate hosts. The materials are designated as: $M1_{1-x-y}RE_xM2_yAl_2O_4$, being M1: Sr,Ca, Ba and M2: Mg, B and
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5 RE a rare earth selected from these list: La, Ce, Pr, Nd, Eu, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu or a
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7 combination of 2-3 rare earths, which act as a dopant. Generally, M1 is strontium and as dopant Eu^{2+} co-doped
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9 with Dy^{3+} .

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12 The first patent related to strontium aluminates was developed by Nemoto & Co. in 1995⁹⁹. They claimed the
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14 invention of a novel phosphorescent phosphor which is completely different from well-known sulfide
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16 phosphorescent phosphors, and has much longer high-luminance afterglow characteristics as compared with
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18 sulfide phosphorescent phosphors which are available on the market. The host material is a compound
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20 expressed by MA_2O_4 , the activator 0.001 mol % to 10 mol % of europium and the co-activator 0.001 mol % to 10
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22 mol % of lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, terbium, dysprosium,
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24 holmium, erbium, thulium, ytterbium, lutetium, manganese, tin or bismuth.

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28 Subsequent, others researcher groups have focused on improving the persistence of the luminescence,
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30 modifying the synthesis. The UGARF (University Of Georgia Research Foundation, Inc.) group include a
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32 quenching step to improve the luminescence response¹⁰⁰. In addition, this group have developed long persistent
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34 alkaline earth aluminate blue phosphors of the general form $MO.mAl_2O_3$ activated by Eu^{2+} in combination with
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36 at least one trivalent metal ion such as Dy^{3+} and orange-red phosphors based on alkaline earth aluminates,
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38 alkaline earth silicates, and alkaline earth aluminosilicates^{101,102}.

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42 Moreover others patents have been centered in decreasing the manufacturing cost. Conventional process
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44 requires a reducing atmosphere at high temperatures (1300-1500°C) and long processing times that increases the
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46 cost of the final product. These process conditions joined with the use of rare earths and grinding steps to
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48 achieve particles with a suitable particle distribution imply costly methodologies. Therefore, some researchers
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50 have focused on conditioning the raw materials to decrease the temperature and the time of thermal treatments
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52 resulting in the reduction of the final price¹⁰³. Following this issue, Shin-Etsu Chemical¹⁰⁴ has developed a
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54 production process for $MA_2O_4:Eu$ type long-lasting phosphor by mixing the recycle waste of alkaline earth
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56 aluminate phosphor with an alkaline earth compound. Long-lasting phosphors are produced at a high cost
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58 because europium, which is an expensive rare earth element, is used as a raw material and in addition,
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1 expensive and high-purity fine-grain type aluminum oxide, alkaline earth carbonate, rare earth oxide are
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3 necessary for obtaining phosphors having a uniform composition. So, by this invention a low-cost production
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5 process was developed.
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8 It is important to remark that the particles obtained by all the patents aforementioned have a particle size
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10 ranging between 10- 1000 μm . As a consequence, sub-micrometer demand is not solved. General Electric Group
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12 reported the possibility to synthesize nanophosphors (including phosphors based on strontium aluminates) (100-
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14 900nm) obtained by sol-gel synthesis. They claimed the use of this option to synthesize different phosphors but
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16 they do not provide results related specifically to strontium aluminates¹⁰⁵.
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19 The main suppliers of long persistent powders are Nemoto & CO., LTD.¹⁰⁶, Honeywell¹⁰⁷ and Jinan Chenghao
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21 Technology Co. Ltd (Chinese company)¹⁰⁸. They offer long persistent powders that emits in a broad range of
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23 wavelengths (green, blue, purple and yellow-orange). Depending on the average particle size the lifetime of the
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25 powder achieves different values. For example the powder denominated PLG-600, which emits in green-yellow
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27 region, has an average particle size 100 μm with a lifetime around 12 hours. Other important Chinese company
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29 in this field is Hangzhou Truth-Chem Co. Ltd. In addition there are some US suppliers as Glonation¹⁰⁹,
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31 Elektrolumens¹¹⁰ and Glowinc¹¹¹ that offers a similar product developed by Chinese companies. Generally, the
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33 manufacturers provide diverse qualities of the product with high long lasting luminescence for powders that
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35 have a particle size $\approx 100 \mu\text{m}$ and with low afterglow response, decreasing the particle size. Green
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37 phosphorescent powders are based mainly on alkaline earth aluminates, and blue and orange-yellow
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39 phosphorescent powders on silicate-aluminate oxides.
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43 ***Luminescence Enhancement: Encapsulation***

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47 Different approaches have been studied to improve water stability including silica encapsulation by a
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49 modified Stöber process to form a silica shell around the phosphors with varying water/TEOS molar ratios⁸³ or
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51 by sol-gel technique¹¹², by direct reactions between triethyl phosphate and strontium aluminate¹⁷, by heating the
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53 mixture of the phosphor and ammonium difluoride (NH_4HF_2) in a covered alumina crucible at 600–700°C for
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55 about 2h¹¹³ and by alumina encapsulation, employing $\text{Al}_2(\text{SO}_4)_3$ and Glycol as disperse medium ¹¹⁴. Therefore,
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57 these encapsulation methods can effectively improve water-resistance of SrAl_2O_4 and the optical properties are
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59 not decreased remarkably after encapsulation.
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5. Applications

Luminescent materials that are responsive to external stimuli have received considerable interest. These materials have been classified on the basis of the types of external stimuli that they are responsive to. If this stimuli is initiated by photoexcitation (excitation by photons), the light emission is called photoluminescence. Within photoluminescence materials, as we said earlier, there are fluorescent and phosphorescent materials, which emit for a short time (10^{-9} - 10^{-7} s) or for a long time ranging from minutes to hours, respectively.

There is still the continuing need for green emitting luminescent materials; the special interest in the green spectral region is related to the luminous efficiency function or eye sensitive function. There are three different vision regimes: *Photopic vision* relates to human vision at high ambient light levels (e.g. during daylight conditions, luminance levels > 3 cd/m²); *Scotopic vision* relates to human vision at low ambient light levels (e.g. at night, < 0.003 cd/m²) and *Mesopic vision* relates to light levels between the photopic and scotopic vision regime (0.003 cd/m² $<$ mesopic luminance $<$ 3 cd/m²). The photopic eye sensitivity function has maximum sensitivity in the green spectral range at 555 nm and the scotopic vision regime occurs at 507 nm. Although the human eye is sensitive to light with wavelengths in the range 390 nm $<$ λ $<$ 720 nm, the sensitivity at these wavelengths is extremely low. Therefore, there is an intense research in materials that the emission wavelengths are centered in green spectral region, but it is arguable due to eye sensitivity becomes more blue-sensitive at lower light levels and the photometric standard does not span the scotopic-mesopic-photopic spectrum^{10,115} (**Fig. 5**).

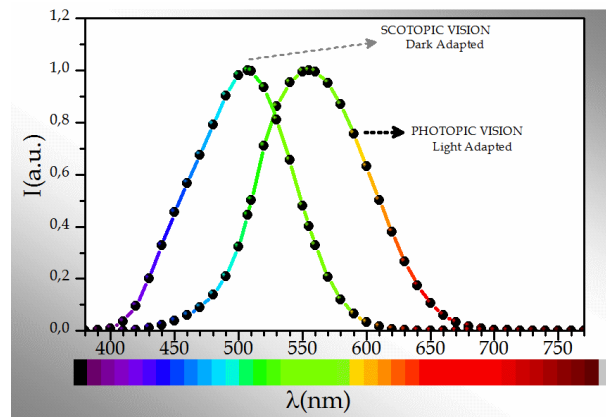


Figure 5. Photopic eye sensitivity function $V(\lambda)$ and the scotopic eye sensitivity function $V'(\lambda)$ values taken from Table 6-1

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1 In addition, long emission lifetimes are also required within a wide range of applications. For that several
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3 green phosphorescent materials have been extensively studied. For this reason, the research has been focused on
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5 SrAl₂O₄ doped with Eu and Dy due to its excellent phosphorescence properties and good stability ¹¹⁷⁻¹²⁰.
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8 The main market of these pigments spans conventional applications as persistent luminous paints employed
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10 for example in the new Nissan Leaf Car¹²¹, that apply UV absorbing glowing paint to a production; inks;
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12 ceramics specifically in vitrified tiles; emergency signs in buildings, highways, construction materials to detect
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14 damages in bridges and textiles for example including these luminescent pigments in polymer melts for the
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16 production of filaments by extrusion processes to warning and security textiles¹²²⁻¹²⁵.
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19 Advanced technologies address some challenges such as: lighting that uses a fraction of the energy; sensors to
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21 detect and identify harmful chemical and biological agents (in *in vitro* and *in vivo* imaging¹²⁶); plasma display
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23 panels, LEDs; security encoding; smart cities, rural lighting. So, these advance luminescent materials have wide
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25 required in displays, defense, medicine, and military fields as well as in our daily life including cosmetic or
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27 dermatological compositions ¹²⁷. Projects as for example Smart Highways by Dutch companies are developing
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29 paints mixing photo-luminescent powder that absorb sunlight in the day and can then glow for up to 10 hours at
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31 night - lighting up the roads at no cost¹²⁸. Moreover, it is possible to enhance the performance by incorporating a
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33 long afterglow SrAl₂O₄:Eu, Dy film. This film acts as efficient light scattering layer on the photoanode to localize
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35 the incident light within the photoanode an increase de light absorption. Recently, this approach has been
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37 employed to improve the efficiency in CdSe quantum dot-sensitized solar cell ¹²⁹. It means that approaches more
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39 sustainable and interactive are being carried out saving energy on signage, buildings, without compromising
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41 safety.
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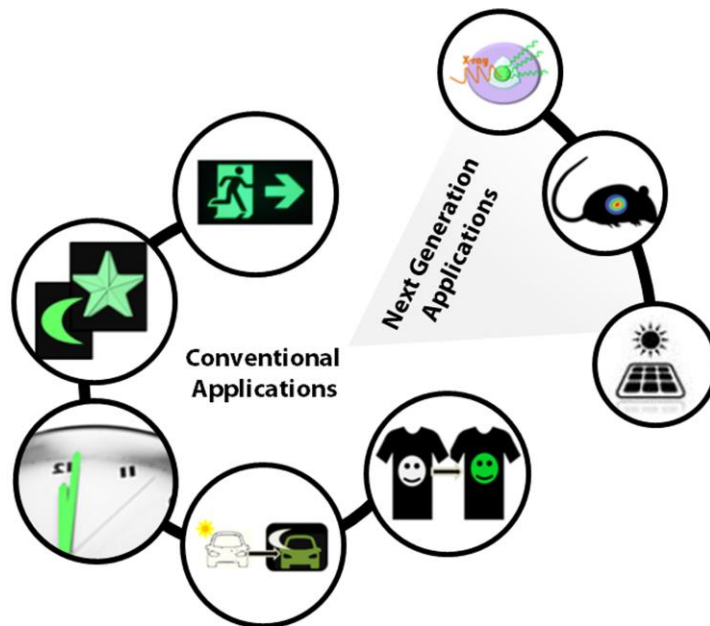


Figure 6. Photopic eye sensitivity function.

The SrAl_2O_4 system doped with rare earth presents long-lasting phosphorescence after the exposure to UV radiation. However, in recent time $\text{SrAl}_2\text{O}_4: \text{Eu}, \text{Dy}$ has been explored as scintillators, finding that emits photons after X-ray irradiation, which makes a potential candidate to easy-use as radiation detection.

Figure 6 offers a succinct picture of the level of commercialization of $\text{SrAl}_2\text{O}_4: \text{Eu}, \text{Dy}$ by application. Main applications at present are in paints, luminous clocks, children's toys, emergency signs, traffic signage and textiles and in lesser extent in paints for automotive industries. Further, the combination of excellent luminescent properties, chemical stability, biocompatibility, and facile integration with flexible technology, makes $\text{SrAl}_2\text{O}_4: \text{Eu}, \text{Dy}$ a candidate material platform for the next generation of ceramics, enamels, glasses, automotive industries and saving energy devices. Considering the wide range of potential $\text{SrAl}_2\text{O}_4: \text{Eu}, \text{Dy}$ applications, the chart of future trends shows the potential markets of the integration of $\text{SrAl}_2\text{O}_4: \text{Eu}, \text{Dy}$ will in medicine, radiation detection and optoelectronics.

6. Limitations of Industrial Phosphors and Outlook

Concerning, phosphorescent materials based on $\text{SrAl}_2\text{O}_4: \text{Eu}, \text{Dy}$ employed in the industry, mainly in emergency signs in buildings and highways, luminous markings in watches and other instruments as dials,

1 luminous paints, the manufacturers employ the powders available in the market. Conventional processing
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3 methods fabricate powders with inhomogeneous particle distributions and with larger particle size ($\geq 20 \mu\text{m}$).
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5 Therefore, to integrate the powder into the final application, the manufacturer should carry out a conditioning
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7 process. Their use in practical applications will follow in near future, so the search for new processing methods
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9 continues and is a technological challenge.

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12 Moreover, in spite of the most demanding applications require powders with sub-micrometer size, the
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14 industry demands more specifically powders that not appear slightly yellow (**Fig. 7**) once are employed in the
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16 final application, for example in a coating. Applications such as emergency signs and traffic signage have a
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18 yellowish color, this coloring can be considered detrimental because of visual impact for esthetic requirements.
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20 As a consequence, efforts should be made to avoid this visual impact, achieving a greater whiteness.
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33 **Figure 7.** Yellowish color of the commercial powders based on $\text{SrAl}_2\text{O}_4:\text{Eu}, \text{Dy}$ supplied from Jinan Chenghao
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35 Technology Co. Ltd
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38 Taking in account all the premises discussing here, the synthesis of sub-micrometric particles for industrial
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40 applications is crucial for the development of advanced applications. Two approaches can be followed; starting
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42 from a bulk material and carrying out a milling process or synthesizing directly submicron particles. As we can see
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44 earlier, there is not still a suitable milling process that avoids the decrease of the photoluminescence response.
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46 The high-energy of the impacts during the milling process generates reactive and amorphous surfaces on the
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48 particles that produce a great deterioration of the crystallinity; meanwhile low-energy dry milled powders have
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50 smooth crystal surfaces, keeping the crystallinity of the particles that avoid a great deterioration of functional
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52 properties. However, the particle size reduction on both cases fails to obtain particles $\leq 1 \mu\text{m}$.
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56 On the contrary, if the material was synthesized in submicron range directly. The surface energy increases
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58 drastically; this aspect has an important influence on surface distortion of the crystalline structure and on the
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1 crystal field change around the dopants positions, Eu^{2+} and Dy^{3+} that derived in luminescence response
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3 decreasing.
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6 Usually, nanophosphors consist of spherical particles but particle morphology has a great influence on the
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8 final properties. For this reason, the research in other morphologies has a promising future. For example,
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10 nanosheets or micro/ nano-structured materials in the form of microscale particles assembled from nanoscale
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12 crystals can both avoid the shortcomings of nanomaterials and retain them to inherit the advantages. These
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14 kinds of structures have good crystallinity and are free of defects, and in addition the photoluminescence
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16 response can be improved due to its large surface to volume ratio with respect to those of bulk materials. It has
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18 been reported some recent publication about phosphor with nanosheet shape but there few report on long
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20 lasting phosphors¹³⁰.
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24 Therefore, obtaining nano-structures would be a good direction to improve the performance of
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26 phosphorescent materials. To create well-defined morphologies, template assisted techniques should be
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28 developed. By hydrothermal route combined with a post annealing process at 1300°C, $\text{BaAl}_2\text{O}_4:\text{Eu}, \text{Dy}$ ¹³¹
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30 nanotubes have been synthesized: obtaining diameters of 100-300nm and lengths up to tens of micrometers.
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32 However, nanostructured $\text{BaAl}_2\text{O}_4:\text{Eu}, \text{Dy}$ showed a faster afterglow decay rate than its bulk counterpart.
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34 $\text{SrAl}_2\text{O}_4:\text{Eu}, \text{Dy}, \text{Ce}$ nanotubes have also been obtained with 90 nm in diameter and 650 nm in length by a
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36 multistep process: (i) annealing at at 1300°C; (ii) Post annealing at 1200°C; and (iii) Mechanical deposition and
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38 dry pressing of the as-synthesized particles on SiO_2 and Al_2O_3 templates ¹³². Moreover $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}, \text{Dy}$
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40 nanotubes (diameter 70-80 nm) have been synthesized by an anodic alumina oxide (AAO) assisted co-deposition
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42 method¹³³. By electrospinning techniques different types of nanofiber were produced based on
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44 $\text{CaSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ¹³⁴, $\text{Ca}(\text{Sr})\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}, \text{Dy}^{3+}$ ¹³⁵, $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}, \text{Eu}^{3+}$ ¹³⁶, and $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}, \text{Dy}^{3+}$ ¹³⁷.
45
46 $\text{S}_3\text{Al}_2\text{O}_6:\text{Eu}^{2+}, \text{Dy}^{3+}$ nanorods have been synthesized by the sol-gel technique combined with a microwave
47
48 assisted approach; obtaining a red long afterglow phosphor¹³⁸. In addition, $\text{SrAl}_2\text{O}_4:\text{Eu}, \text{Dy}$ nanosheets (widths of
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50 100 nm and a length of 1 μm) were produced by an hydrothermal route in an autoclave at 160 °C for 24 h and
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52 after a post-annealing at 1300 °C for 2 h under a reducing atmosphere of active carbon. However, the
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54 $\text{SrAl}_2\text{O}_4:\text{Eu}, \text{Dy}$ nanosheets decayed more rapidly than commercial powders prepared by solid-state reaction¹³⁰.
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1 So the design of scalable process of self-supported micro/nanostructures onto microscale particles as fragments
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3 of a puzzle would be a good direction to improve the performance of phosphorescent materials.
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6 In addition, for various industrial applications such as device fabrication and surface coatings it is also
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8 important to investigate these phosphors in the form of thick and thin films. Thin films of SrAl_2O_4 have been
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10 prepared by RF sputtering¹³⁹, by pulsed ion beam evaporation (IBE)¹⁴⁰ to avoid sample annealing to crystallize
11
12 the SrAl_2O_4 phase as in RF sputtering method and by the pulsed laser deposition (PLD)^{141,142}; obtaining in the
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14 later method 30-35 nm nanostructured layers. However, these studies are preliminaries because almost the un-
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16 annealed films were all amorphous and it is necessary to optimize the film growth, so a carefully selection of
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18 deposition conditions should be address. The film growth can be controlled by the condition of the flux
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20 generation and its propagation, the substrate and its location, parameters that severe influence on the PL
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22 properties of the film.
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26 On the basis of above discussion, one major challenge for the long lasting luminescent materials science
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28 community is to devise methods to synthesize materials with tunable size, shape, desirable surface characteristic
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30 as well as the development of approaches that allows tailored emission color and enhanced conversion
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32 efficiency.
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35 An important attention is placed on the integration of different functionalities for providing solutions in
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37 specific applications domains, such as biological imaging, molecular detection, drug delivery and
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39 optoelectronics. Therefore, the persistent luminescent research should deliver innovative, sustainable and cost
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41 effective materials solutions for the reduction of rare earth elements used in luminescent materials due their
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43 scarcity¹⁴³.
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46 Quenching of luminescence is inevitable, leading to an efficiency that is smaller than that using its bulk
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48 counterpart¹⁴⁴⁻¹⁴⁶. An effective solution is to grow epitaxial shell layers by which the surface quenching effect can
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50 be largely minimized; generating for example core-shell structures.
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54 Moreover, surface-protection strategies should be addressed extensively to enhance the external layer
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56 response¹⁴⁷⁻¹⁴⁹. In addition, the harmful collateral effect of nanotechnology must be addressed by using new safe
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58 by design micro/nanostructures which provides advantages of nanoparticles avoiding harmful effect.
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1 SrAl₂O₄:Eu,Dy powders are widely employed and also there is an increase in research toward synthesizing
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3 high performance material in emerging technologies such as digital printing, electronic displays, solar cells¹²⁹
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5 and scintillators (widely utilized for radiation detection and in elementary particles discoveries, led to a
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7 breakthrough in their efficiency, which combines both high light output and decay time)^{150,151}. Moreover, it is
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9 important to remark their use in functional pigments and the possibility to generate inks and create micrometer
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11 sized quick response codes through assemblies for security printing field¹⁵². Therefore, the research in these
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13 materials has still a promising future.
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17 In addition, persistent luminescent materials for innovative power components are demanded to develop
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19 sustainable materials, architectures and processes for power electronics suitable for use in energy technologies,
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21 contributing to the future of Smart Cities, bearing in mind that for example in construction materials, still under
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23 discussion the stability of aluminates at higher temperatures.
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25 26 27 **7. Conclusions**

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29 Long- lasting luminescent materials have become the international research frontiers and focuses in the field of
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31 high technology and new materials. In this paper, we have systematically reviewed the developments of
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33 different synthesis methods as well as its persistent luminescence properties of SrAl₂O₄ -based materials, and
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35 some suggestions on the future development of SrAl₂O₄ materials were also addressed. Several approaches have
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37 been developed to provide a steady supply of SrAl₂O₄:Eu²⁺, Dy³⁺ in large areas and quantities, amenable for
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39 mass applications. However, the most demanding applications require powders with specific requirements that
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41 are not available in the market. It is clear that large-scale production is needed for the widespread application of
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43 this material.
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47 The design of nanostructured SrAl₂O₄:Eu²⁺, Dy³⁺ materials allows to obtain different morphologies and as
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49 consequence different photoluminescent responses. Moreover, the reduction of temperature, duration of the
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51 thermal treatment and the precursor's materials needed imply the decrease of the material economic cost.
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54 The limitations founded in the present state of the art allow establishing the main issues that should be
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56 addressed. The proposed solutions go well beyond the state of the art and it should be demonstrated that
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58 materials with improved durability also fulfil all properties necessary for the future applications. Exploitation
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1 potential of the proposed solutions compared to state-of-the-art solutions currently available will be open new
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3 tendencies to develop these persistent materials. As a result, we can believe that the nanostructured
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5 SrAl₂O₄:Eu²⁺, Dy³⁺ materials allows will get widely practical applications in the near future.
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