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Long lasting phosphors: $SrAl_2O_4$: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 $SrAl_2O_4$: 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 that their predecessors. For that, large attention has been paid to the development of an efficient preparation method of $SrAl_2O_4$ 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 $SrAl_2O_4$-based materials.

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 proteins [1], organic pigments [1], metal complex [2,3], semiconductors [4] 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

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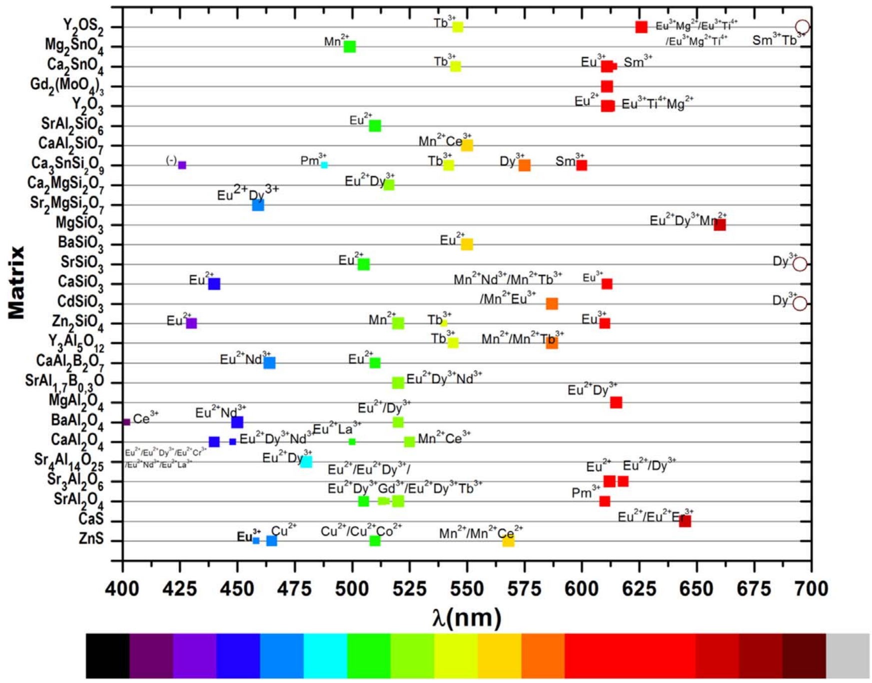

Fig. 1. Overview of the compounds that exhibit persistent luminescence: The vertical axis collects different matrix and the horizontal axis symbolize the electromagnetic spectrum in the visible range. Inside the chart, there are data points related to the chemical elements that dopes the matrix (host)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

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

2.1. 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 higher [7].

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: intraconconfigurational d→ d (Mn^{2+}, Cr^{3+}) or 4 f→ 4 f (Eu^{3+}) or interconfigurational (4 f→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 ions [7–9].

2.2. 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: Measurement and marking at the producer" [11]. This regulation establishes the luminance at the following intervals after the exposure lamp is switched off: 10, 60 and 520 min. In each case the samples are irradiated 10 min by a Xe Arc Lamp (1000 lx).

Generally speaking, there is not a standardized way of measuring and defining persistent phosphors properties. Nonetheless, the majority of decay curves are taken when the sample is irradiated with monochromatic light at 350, 365 and 375 nm during 5 and 10 min [12–19] and by a solar simulator in a lesser extent [20].

3. Persistent luminescence materials

Persistent luminescence materials frequently consist of an inorganic matrix (known as host) and activated 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+}, 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+}. This active center can act as emitter or trap: the role of the emitter is giving radiation after the excitation and the trap stores the excitation energy. However, there still exists strong disagreement on the exact trapping mechanism for the most studied type of persistent luminescent materials.

Fig. 1. provides an overview of the compounds that exhibit persistent luminescence. This chart has been made taking in account the main compounds taken from the literature [5,21–45]. The vertical