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Role of oxidizing agent to complete the synthesis of strontium aluminate based phosphors by the combustion method

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Abstract

The influence of processing parameters on phase formation of strontium aluminates doped with Eu^{2+} and Dy^{3+} by the combustion method has been evaluated. The addition of a slight excess of urea as fuel has an important effect on the phase formation, but a larger amount of urea inhibited the strontium incorporation into the stuffed tridymite-like structure. The experimental results show that it is possible to incorporate larger amount of urea than the theoretical one by adding nitric acid as oxidizing agent. The presence of an oxidizing agent promotes both an effective chelation of the cations and a higher crystalline order on strontium aluminate. Nanostructured lamellar particles have been obtained in a single step and the particles are well crystallized. The combustion method avoids the standard requirements of post-thermal treatments in reducing atmosphere to promote the appearance of Eu^{2+} cations. A higher amount of urea in the presence of the oxidizing agent produces strontium aluminate particles with higher phosphorescence brightness, owing to the increase of the reduction process Eu^{3+} to Eu^{2+}. The luminescence properties correlate with the crystallite size of the strontium aluminate. The results demonstrate a pathway to obtain phosphorescent pigments with size down to 10 µm.

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1. Introduction

Phosphorescent materials have been studied due to their potential application in different areas like traffic safety and emergency signs, clocks, fluorescent devices and inks. After the discovery in 1996 of $SrAl_2O_4$: $Eu^{2+}Dy^{3+}$ as new persistent luminescent compound by Matsuzawa et al. [1], many researchers have developed some methods for preparation of strontium aluminate powders including sol-gel method, hydrothermal synthesis, chemical precipitation, solid-state reaction and so on. In recent years, rare earth-doped strontium aluminates have been intensively researched for their quantum efficiency, good stability, long-lasting time, which implies a wide application in many areas [1–3].

Commonly strontium aluminates are produced by solid state reaction, due to the refractoriness of alumina compounds; this method requires high temperatures, around 1300 – 1500ºC**,** and a long processing time. Some researchers included the addition of mineralizing agent as boron to decrease the synthesis temperature [4,5], nevertheless, the powders produced by this synthesis route have a particle size within the range of 20 to 100 μm [6]; being a disadvantage for some applications. It is known that luminescent properties depend considerably on the grain size. New attractive applications will be possible if the grain size decreases down to 10 μm, particularly those related to printing technologies.

Among the different synthesis methods, $SrAl_2O_4$: $Eu^{2+}Dy^{3+}$ phosphors have been prepared by combustion method [7–9]. This method is suitable to obtain these functional materials due to some advantages such as low processing temperature and fast synthesis. In addition, this method produces a submicron grain size. For these reasons this synthesis method has been considered in order to obtain these phosphors. One of the advantages of the combustion method is the low temperature of synthesis. It has been reported that at initiating temperature of 500ºC the $SrAl_2O_4$ a monoclinic phase begins to appear. Nonetheless, other references denote the optimal temperature should be 600ºC to achieve the best optical properties [10,11]. It is necessary to take into account that $SrAl_2O_4$ has two polymorphs: monoclinic symmetry that it is stable at temperatures below 650ºC and hexagonal symmetry that it is stable above this temperature. Monoclinic phase shows the luminescent properties; however, there is not a clear agreement about the emission efficiency of the hexagonal structure in this system.

In the combustion method, the role of the fuel in the fulfillment of the synthesis has been investigated. Generally urea, $CO(NH_2)_2$, is the fuel used and some authors concluded that an excess urea should be required. The optimal quantity of urea is 1.5 times the theoretical one [10] considering that with low concentration of urea a complete reaction of raw materials it is not attained, while if the quantity is too high, the $SrAl_2O_4$ monoclinic structure does not synthesize. The maximum amount of urea it is limited to 2.5 times the theoretical one because the hexagonal phase becomes to appear when a higher quantity of urea are added [11].

The theoretical or stoichiometric amount of urea is calculated from the combustion reaction equation following this equation:

$$3Sr(NO_3)_2 + 6Al(NO_3)_3.9H_20 + 20CO(NH_2)_2 \rightarrow 3SrAl_2O_4 + 94H_2O + 20CO_2 + 32N_2 \quad (1)$$

The incorporation of an excess of urea excess implies the contribution of other terms in the above equation

$$3Sr(NO_3)_2 + 6Al(NO_3)_3.9H_20 + 20\cdot m\ CO(NH_2)_2 + 30(m-1)O_2 \rightarrow 3SrAl_2O_4 + (40\cdot m + 54)\ H_2O + 20\cdot m\ CO_2 + (20\cdot m + 12)N_2 \quad (2)$$

where m denotes the urea ratio. An excess of urea implies therefore a higher consumption of oxygen in order to complete the reaction. To optimize the combustion synthesis an oxidizing agent as nitric acid could be particularly relevant.

Therefore, in this work different urea amount in the combustion synthesis of $SrAl_2O_4$: $Eu^{2+}Dy^{3+}$ are used and it carried out a study related the effect of nitric acid incorporation. The use of oxidizing agent could improve the reaction completion as well to tailor phosphorescent properties. The correlation between combustion process, morphology and optical properties of strontium aluminate based particles is discussed.

2. Experimental details

$SrAl_2O_4$: Eu^{2+}, Dy^{3+} particles were synthesized via solution combustion synthesis. The solution was prepared by dissolving $Al(NO_3)_3{\cdot}9H_20$ (Merck, 98.5%) in deionized water and $SrCO_3$ (Merck, 99.9%), Eu_2O_3 (Metal Rare Earth Limited, 99.5%) , Dy_2O_3 (Rare Earth Limited, 99.5%) in nitric acid HNO_3 (Sigma-Aldrich, 65%) to form nitrate solution. The above materials were mixed according to the chemical formula $Sr_{1-x-y}Eu_xDy_yAl_2O_4$, where x = 0.02 and y= 0.01. During the 30 min under heating at 80 ºC the solution was stirred, after that, the quantity of urea was added. The full precursor solution dried at 100ºC in a porcelain crucible with a glass-watch lid. The solution was introduced into a furnace maintained at 400ºC and heated up to 600°C; where the ignition took place in a few minutes (CA. 10 min). A white powder with an extremely porous and foam structure was obtained. Selected synthesized powders were also thermally treated at 600 or 900ºC in a furnace under argon atmosphere to improve the luminescent properties.

Phase identification of the powders was determined by X-ray diffraction analysis using a Bruker diffractometer (D8, Bruker, Germany) using Cu Kα. The microstructure of the samples was evaluated using secondary electron images of field emission scanning electron microscopy (FESEM, Hitachi S-4700). Image analysis of FESEM micrographs was used to determine the grain evolution by using an Image analysis program (Leica Qwin, Leica Microsystems Ltd, Cambridge, England) considering more than 100 grains in each measurement. Optical properties of these materials by measuring emission and excitation spectra were investigated. The photoluminescence spectra of the phosphor particles were recorded with a spectrofluorometer (Fluorolog®-3, HORIBA Jobin Yvon) at room temperature. The luminescence intensity was measured over the wavelength 425–650 nm, a Xenon arc lamp was used as excitation source (λ_{exc}= 380nm and 464nm). The decay profiles were also recorded using the same instrument after the samples were sufficiently excited for about 5 min.

3. Results and discussion

3.1. Influence of the ratio of urea on the synthesis

Structural characterization

Concerning the combustion synthesis, the urea content and the oxidizing agent ratio are studied. X -ray diffraction patterns of the combustion powders by using the stoichiometric amount of urea, m=1 and excess, m=2 and 3, are shown in Fig. 1. The combustion reaction for m=1 produces a powder which XRD patterns show major crystalline phase as unreacted raw materials and minor presence of $Sr(NO_3)_2$. The main appearance of $SrCO_3$ indicates the carbonation of the nitrate species owing to the reaction medium created by carbon dioxide during the combustion. The peaks of $Sr(NO_3)_2$ are related to starting $Sr(NO_3)_2$, indicating that the reaction is uncompleted in agreement with previous reported result [10-13]. It is important to understand the influence of the fuel ratio in the chelation of the cations. Less urea than required impedes the fully chelation of cations. For this reason, some Sr cations remain un-complexes. During the combustion it is formed incipient $SrAl_2O_4$ monoclinic phase, space group $P2_1$, characterizes by three peaks in the 28-30° 2θ accordingly withJCPDS (No. 34-0379). In addition, two other crystalline phases with different Sr/Al ratio appear, $Sr_3Al_20_6$ and $Sr_4Al_{14}O_{25}$. Following the reaction (1), the strontium aluminate based materials grows as a minority phase when a stoichiometric amount of urea is employed. The presence of crystalline phases having different Sr/Al ratio reveals the lack of homogeneity in the system during the combustion process.

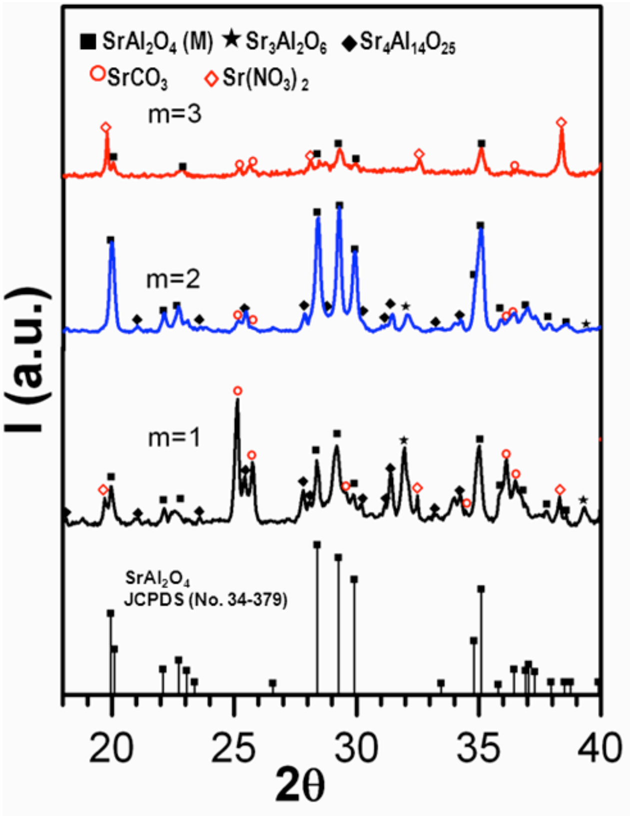

Figure 1. XRD patterns corresponding to the combustion products obtained, including different urea amounts, m= 1, 2, 3.

The increase of urea to m=2 leads mainly to the main formation of the monoclinic phase, and minority secondary phases as $Sr_3Al_2O_6$ and $Sr_4Al_{14}O_{25}$. The presence of these phases is again attributed to the characteristic lack of energy homogeneity during the combustion reaction [12]. The $Sr_3Al_2O_6$ phase appears at lower temperature in the $SrO-Al_2O_3$ system than $SrAl_2O_4$ phase [6]. The amount of $Sr_3Al_2O_6$ decreases when the urea amount increases. The appearance of $Sr_4Al_{14}O_{25}$ can be associated to the reduced temperature range of stability for the monoclinic polymorph phase [13]. Minor presence of $SrCO_3$ is also formed in the m=2 sample.

The powders synthesized by using large amounts of urea, m=3, failed to form the monoclinic phase., Fig. 1 according with previously reported results [10,11]. The main crystalline phase is Sr $(NO_3)_{2,}$ this fact indicates that the oxidizing/reducing character of the mixture directly influence the preferential chelation of some cations, as has been reported previously in other systems[14]. As a consequence, it is reasonable to consider that the urea preferentially chelates strontium cations. The presence of $Sr(NO_3)_2$ correlated this assumption because un-chelated nitrate crystallize during heating. Moreover, the presence of crystalline phases reduces for higher amount of urea, Fig.1. The presence of large amounts of urea can somehow interfere in the complexation step; resulting in a heterogeneous combustion reaction, with unburnt fuel. The urea is a reducing agent, when incorporates in the reaction required an oxidizing agent to complete the combustion reaction. In a standard procedure, the oxygen of the medium plays this role but if the ratio of urea increases greatly the diffusion of oxygen of the medium is not fast enough to complete the reaction and as a consequence, the phase formation decreases. The maximum amount of urea to be incorporated in the combustion reaction has been established as 2.5 times the stoichiometric amount in order to achieve the formation of monoclinic phase [15].

3.2. Synthesis combining an extra step of calcination.

Structural and optical characterization.

The emission spectrum of $Sr_{0,97}Al_2O_4$:$Eu_{0,02}$, Dy $_{0,01}$ synthesized by the combustion method by using m=1 and 2 compositions are shown in Fig. 3. The emission band centered at 510 nm is assigned to the spin-allowed transition of $4f^65d^1 \rightarrow 4f^7$ ($^8S_{7/2}$) of Eu^{2+} ions and the emission located at 611 nm correspond to the spin-forbidden transition of $^5D_0 \rightarrow {}^7F_2$ for the Eu $^{3+}$ ions [16]. The green-emitting intensity increases when the amount of urea increases to m=2 because the formation of monoclinic phase is higher and the presence of precursor materials diminished, Fig. 3. The emission at 611 nm is more relevant in m=1 compositions, Fig. 3 inset. Besides this fact, the urea possesses two roles: one is to allow the reaction to take place and the second one is a chelating agent. Moreover, it is important to remark that combustion method avoid the use of a reducing atmosphere during the thermal treatment due to the fuel burn out. For this reason the intensity of the peaks corresponded to Eu^{3+} decreases for m=2 but increasing the monoclinic phase formation fails to reduce Eu^{3+} completely into divalent Eu^{2+}.

To improve the luminescent properties of phosphors synthesized by the combustion method with m=2 a further thermally treated in Ar_2 atmosphere at 600ºC and 900ºC during 1 hour is attempting to evaluate the luminescence and its correlation with the presence of Eu^{2+}. As can be observed in Fig. 3, luminescence related to Eu^{3+} decrease for materials thermally treated at 900ºC. These results are in agreement with the fact that the thermal treatment occurs in a graphite chamber furnace. Moreover, the structural defects decrease during the thermal treatment and the powders acquire higher crystallinity. As consequence the luminescence increases, Fig.2. XRD pattern shown diffraction peaks in the 28–30.5° 2θ range having a background that reveals the existence of a certain degree of amorphicity. This background located decreases with the thermal treatments. The diffraction peaks belonged to the crystallographic plane (-221) located at 29º 2θ increase with the thermal treatment, being this diffraction peak the preferential growth direction, Fig.2.

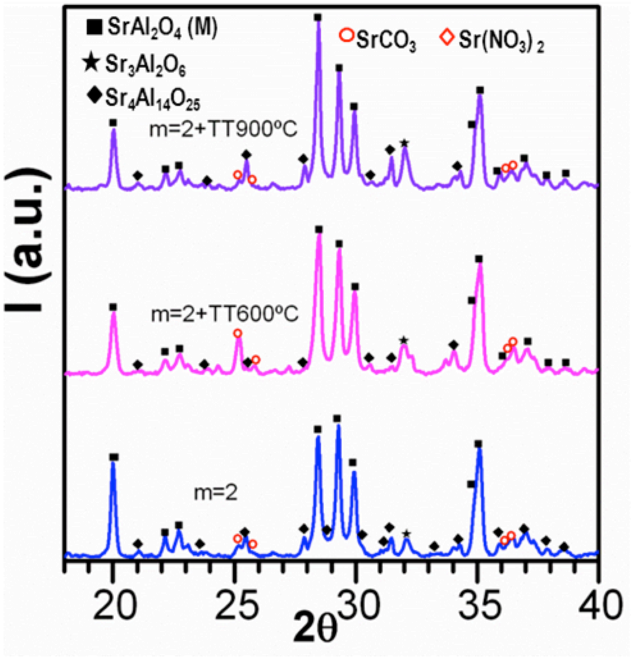

Figure 2. XRD patterns corresponding to the combustion products obtained, including urea content of m= 2. Powders m=2 are thermally treated at 600°C and 900°C in Ar_2 atmosphere and denoted on the graph as m=2 +TT600ºC and m=2 +TT900ºC respectively.

The crystallite size (D) of the powders is as estimated from the full width at half maximum of the diffraction peak by the Sherrer's equation:

$$D = \frac{K\lambda}{B\cos\theta} \qquad (2)$$

where λ is the X-ray wavelength, B half maximum of the diffraction peak, θ is the angle of diffraction, and using a shape factor (K) of 0.9. The indexed diffraction peaks (-221), (220), (211) and (031) for the monoclinic phase crystallite sizes are selected to calculate the crystallite size. Crystallite size of ca. 33 nm and 34 nm are obtained for the powder synthesized using m=2 and the same powder additionally thermal treated at 600ºC, respectively. The crystallite size slightly increases from ca.33 nm to.38 nm for the powder additionally thermal treated at 900ºC. The increase of the luminescence after thermal treatment at 600°C is very weak if compared to the powder treated at 900°C, indicating that higher crystallinity improves the optical properties, as shown in Fig. 3. Slight shifts in the emission band may be attributed to the changes of the crystal field around Eu^{2+} [9,17] where the defects migrate near the Eu^{2+} activators to become electron traps [18]. The presence of Eu^{3+} does not reinforce the role of Eu^{2+} to attract anion vacancies that it is more efficiently played by the co-dopant Dy^{3+}. The large increment in luminescence after thermal treatment at 900°C denotes not only a complete reduction of europium cation but a vacancy migration toward Eu^{2+} which it is more efficient for increasing luminescence emission as occurs in solid state synthesized powders [9]. Therefore, a better diffusion of cations it is required to improve phosphorescence properties.

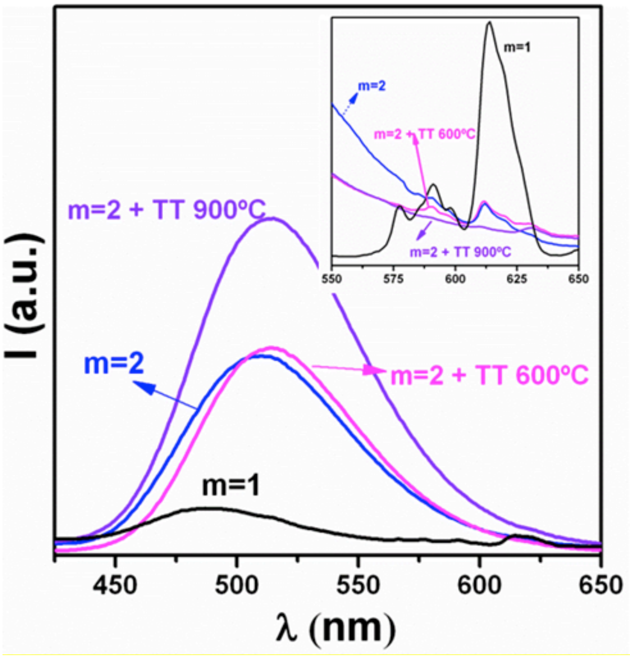

Figure 3. Emission spectra upon excitation at 380 nm and 464 nm (inset) of the $Sr_{0,97}Al_2O_4:Eu_{0,02}$, Dy $_{0,01}$ powders synthesized by combustion method with urea ratio of m=1 and 2. Powders m=2 are thermally treated at 600°C and 900°C in Ar_2 atmosphere and denoted on the graph as m=2 +TT600ºC and m=2 +TT900ºC respectively.

3.3. Influence of the nitric acid addition to the synthesis

Structural characterization

In order to attain a complete combustion reaction, here we proposed the nitric acid addition as internal oxidizing agent. The nitric acid content required by the following equation is calculated:

$$5CO(NH_2)_2 + 6HNO_3 \rightarrow 5CO_2 + 13H_2O + 8N_2 \qquad (3)$$

The urea in the system requires a stoichiometric amount of nitric acid accordingly to the above equation. Fig.4a shows the XRD patterns of the $SrAl_2O_4$ powders synthesized by combustion process when incorporates nitric acid as an oxidizing agent with urea contents of m=3, 4 and 5, and initiation combustion temperatures of 400, 500 and 600ºC. At 400ºC, the powder achieved poor ignition accordingly by the presence of, impurity phase, $Sr_3Al_2O_6$, with mayor $SrAl_2O_4$ phase. The impurity phase decreases at 500ºC and almost disappears , when the ignition temperature increases to 600ºC, where the mainly phase is $SrAl_2O_4$. The XRD pattern of strontium aluminate based powders synthesized by the combustion process with urea content corresponding to m=3, 4 and 5 and incorporating nitric acid as oxidizing agent are shown in Fig.4 (b). The monoclinic phase clearly is the major crystalline phase in all cases. As increasing the urea content in the presence of the oxidizing agent the monoclinic phase of $SrAl_2O_4$ is enriched as well their crystallinity. Moreover, the decrease of the background below main diffraction peaks at 28–30.5° 2θ, previously commented for the powder m=2, suggests the formation of $SrAl_2O_4$ powder with enhanced crystallinity. $SrAl_2O_4$ crystallite size increases from 36 nm for the powder with urea content corresponding to m=3 to ca. 45 nm for the powder with urea content corresponding to m=5. The introduction of nitric acid allows the use of higher fuel amount and therefore the combustion temperature is more homogeneous and higher in all the powder during the combustion. The presence of secondary phases as unreacted $SrCO_3$ or non-stoichiometric strontium aluminate phosphors as $Sr_3Al_2O_6$ and $Sr_4Al_{14}O_{25}$ diminished progressively with the amount of fuel. It is very important to remark here that it is possible to obtain monoclinic strontium aluminate powders by increasing the amount of urea if the nitric acid is used. In our knowledge the proposed reaction is used in this system for the first time. The absence of oxidizing agent in the combustion process is one of the reasons to fail in the formation of the monoclinic phase, which has a higher light emission efficiency than the hexagonal one [19].

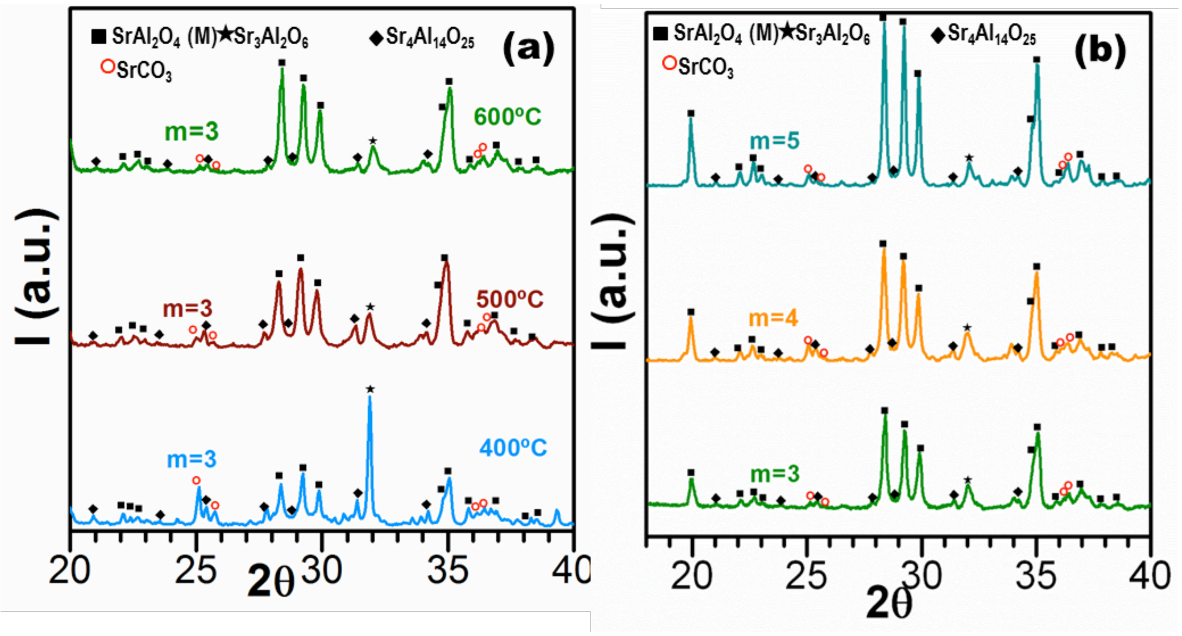

Figure 4. XRD patterns of $SrAl_2O_4$:Eu, Dy phosphors synthesized by the combustion process by adding HNO_3: (a) urea amount of m=3for, ignition temperatures of synthesis in 400, 500 and 600ºC (b) Ignition temperature of 400ºC for different urea amounts, m=3, 4 and 5.

The FTIR spectra for the powder obtained using the urea content of m=3, 4,5 + HNO_3 is shown in Fig. 5. A broad band appears at 3436 cm^{-1}((Fig. 5 inset (b)) corresponding to vibrations of free and hydrogen-bonded hydroxyl groups due to the air exposure [20]. This band is weak, therefore it suggest that the surface of phosphors has low water absorption from the environment. The band located at 1448 cm^{-1} could be assigned to strontium carbonate formed during the reaction [21]. The weak absorption band at 1363 cm^{-1} could be associated with the stretching vibration of the N-O group; the origin of this band is due the nitrate content of the raw materials [22]. The inset (b) in Fig.5 reveals that higher urea content, m=4, 5 + HNO_3, result in higher definition of infrared bands in comparison with the powder obtained from lower urea content, m=3+ HNO3. This result agrees with a higher degree of crystallinity in powder synthesized with higher amount of fuel combined with oxidized agent. In the 1000–600 cm^{-1} spectral range the occurrence of multiple bands required a de-convolution procedure to resolve the presence of different bond groups. The FT-IR spectrum de-convolutes in isolated IR bands by assuming they have a Gaussian profile and these bands correspond to the characteristic vibrations of Al–O, Sr–O and Sr–O–Al bonds. The spectrums are normalized to 639 cm^{-1} band. The observed specific peaks at 842, 785, 655 and 639 cm^{-1} are assigned to some stretching vibrations of the AlO_4 tetrahedra in $SrAl_2O_4$ [23,24], 740 and 693 cm^{-1} are attributed to AlO_4 tetrahedra in $Sr_3Al_2O_6$ and 893, 869, 803, 768, 711, 672 and 612 cm^{-1} must be assigned to the Al-O stretching modes [25]. Fig. 6 shown a detail of the evolution of the isolated IR bands. The increase in urea content induces changes in the intensity

The area of the peaks at 639, 785 and 842 cm^{-1} as a function of the urea content shows a linear trend and the area increase with the urea content. These bands assigned to $SrAl_2O_4$ formation demonstrate that higher urea content enhanced the monoclinic phase as well their crystallinity. On the other hand, the peaks assigned to AlO_4 tetrahedra in $Sr_3Al_2O_6$ decrease with the urea content as an indication of the secondary phase decreasing in agreement with the results obtained by XRD.

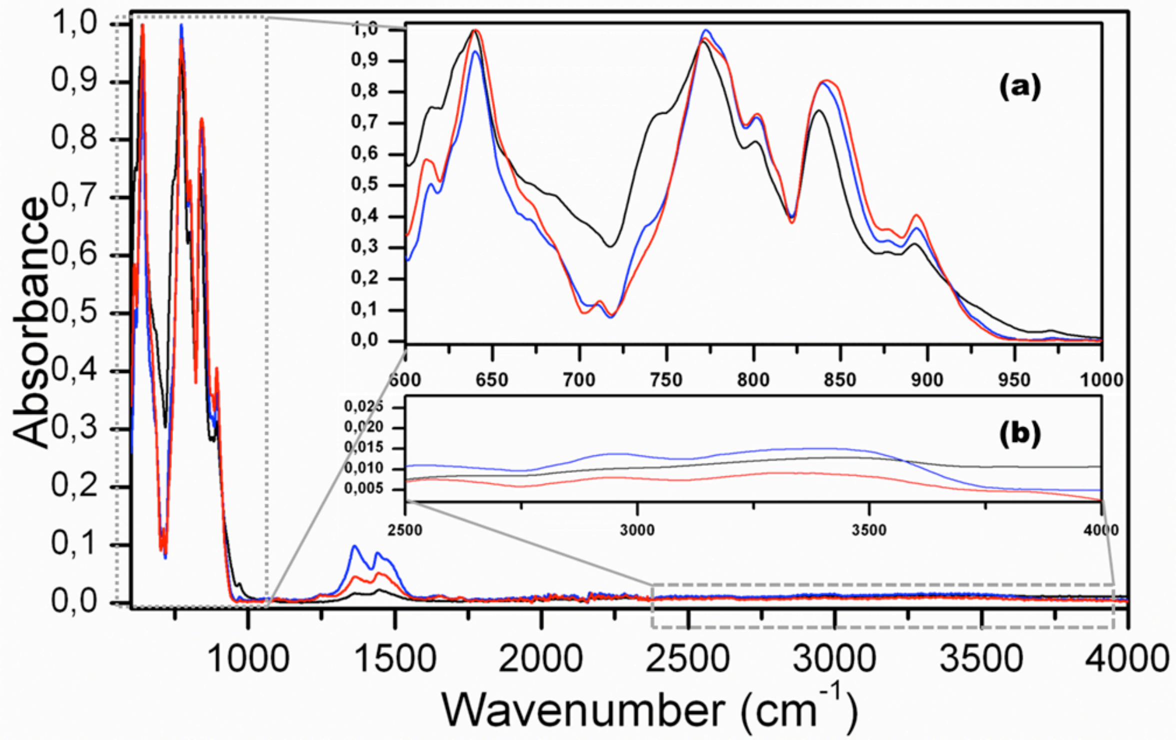

Figure 5. Infrared spectra in the 4000-600 cm^{-1} spectral range of phosphor powders obtained by combustion method using the urea content of m=3, 4,5 and HNO_3 in excess. The insets show details of (a) the 1000-600 cm^{-1} spectral range and (b) in the 4000-2500 cm^{-1} spectral range

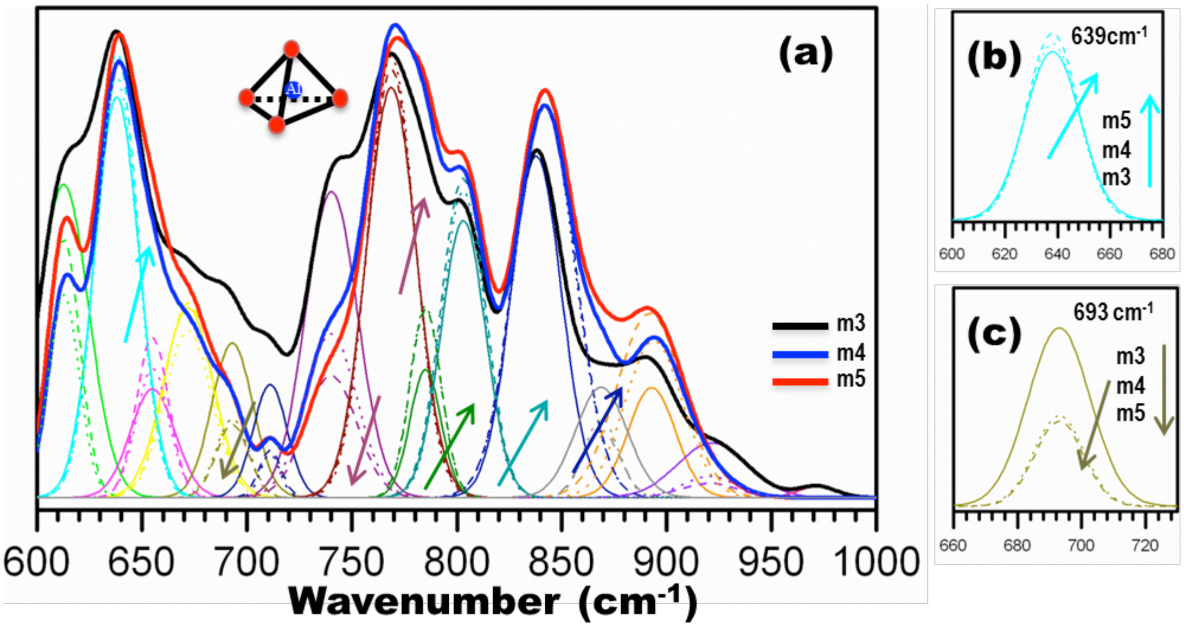

Figure 6. (a) De-convolution of 1000-600 cm^{-1} spectral region for phosphor powders obtained by combustion method by using urea content m =3, 4,5 and HNO_3 in excess. The ticker solid lines correspond to the fitting spectra by the sum of the de-convoluted bands. De-convoluted bands of the powders assigned to me =3, m=4 and m=5 are represented as solid lines, dotted lines, and dashed lines, respectively. **(b)** 639 cm^{-1} bands increasing as a function of the urea content and **(c)** 693 cm-1 decreasing as a function of the urea content.

Optical characterization.

The emission spectra of powders synthesized, including urea content of m=3, 4 and 5 in conjunction with HNO_3 are shown in Fig. 7. The higher urea content in combination with HNO_3 the higher the emission band. The emission intensity is also larger than the one obtained after thermal treatment of powders processed without oxidizing agent. The emission band is located in a similar position than the one obtained after additional thermal annealing in reducing atmosphere. This fact indicates a similar crystal field around Eu^{2+}. It is worth remarking that the result here reported provides the possibility for the preparation of phosphors in a single step without a posterior thermal treatment in reducing atmosphere. The intensity of emission increases greatly for urea content of m=5 in presence of oxidizing agent, see Fig. 7, as a proof that higher combustion energy, improves the crystallinity of the powders. The HNO_3 as an oxidizing agent proportionate the oxygen required for the equation (3) to complete the formation of the monoclinic phase. The inset of Fig. 7 shown the photoluminescence intensity, I_{PL}, as a function of the crystallite size D. It is worth to notice an almost linear increasing of the luminescence properties with the crystallite size.

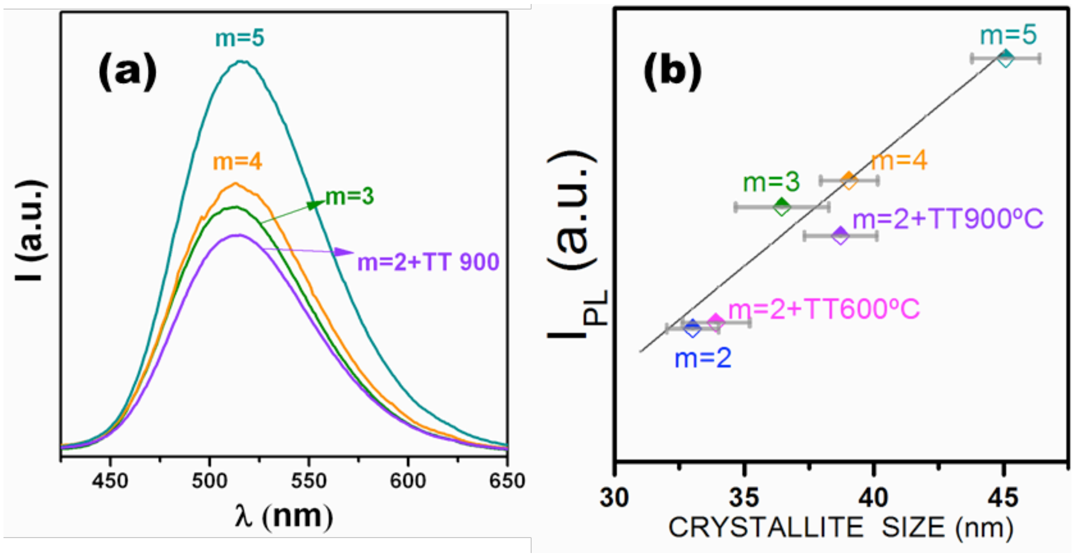

Figure 7. (a) Emission spectra upon excitation at 380 nm of the Sr$_{0,97}$Al$_2$O$_4$:Eu$_{0,02}$, Dy $_{0,01}$ synthesized by combustion method using the urea content of m=3, 4 and 5 and HNO$_3$. For comparison purposed the emission spectra of m=2 as obtained and thermally treated at 600ºC and 900°C in Ar$_2$ atmosphere, denoted as m=2, m=2+TT600 and m=2+TT900, are also represented; **(b)** Photoluminescence intensity as a function of the crystallite size for the different powders.

Fig. 8 shows the decay curves of the afterglow phosphorescence of the powders synthesized. The powder is irradiating for 10 min at 380 nm. After the light source cutoff the phosphorescent decay is measured. The phosphorescent decay time follows an exponential law [26]. . Decay curves fit two exponential components following equation:

$$I = A_1 \exp\frac{-t}{\tau_1} + A_2 \exp\frac{-t}{\tau_2} \tag{4}$$

where I represents the phosphorescent intensity, A$_1$ and A$_2$ two constants, t is the time, τ_1 and τ_2 are the decay times for the exponential components. The phosphorescence initially decays faster than subsequently. The fitting results of the parameters of τ_1 and τ_2 are shown in Table 1. The decay constant, τ_2, increment with the urea content, indicating that the powders have the better decay characteristic. Subsequently, with increasing the urea content in presence of oxidizing agent, the degree of crystallinity increases and the persistent luminescence improves accordingly.

	τ_1(s)	τ_2(s)
m=3	15	72
m=4	15	76

m=5	15	87

Table. 1. Decay times of the phosphorescence of strontium aluminate powder doped with EU and Dy obtained by the combustion method with an excess of urea and oxidizing agent.

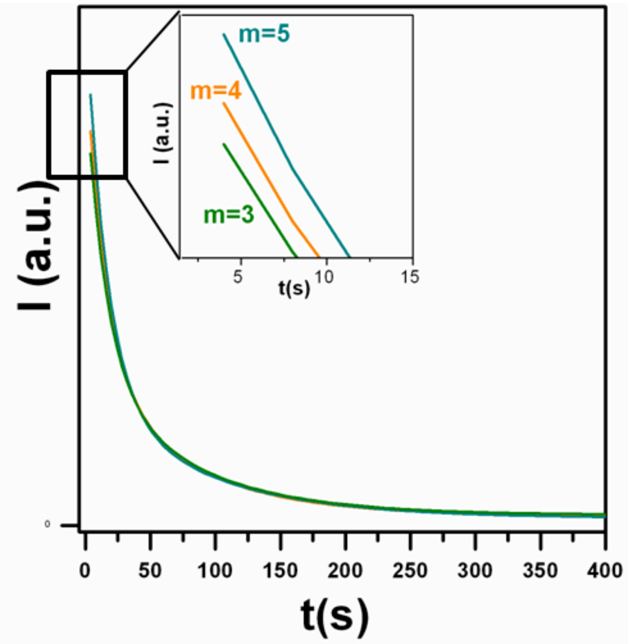

Figure 8. Decay curves, which correspond to phosphor powders obtained by the combustion method with different urea content in presence of oxidizing agent.

Microstructural characterization

The increasing in phosphorescence is a clear advantage for the powders obtained by the combustion method by using urea in combination with oxidizing agents. The increasing correlates with the major presence of monoclinic phase, but the microstructure could possess a relevant effect on such behavior. For such reasons, a morphological analysis of the synthesized powders by FE-SEM is attempted. Fig9. a shows the microstructure of powders produced by combustion method with the urea content of m =3 and HNO_3. The morphology consist mainly of flakes having different sizes ranged from 5 to 25 μm in their largest dimension. The flake type morphology is characteristic of the combustion method [27]. The average thickness of the flakes is ≤ 1 μm, Fig. 9b-c. Such a thickness opens the possibility to use such powders in applications that required low particle size. Moreover, an additional feature of the flake powders is their nanostructure, Fig.9c-d. The flake powders have voids and pores originated by the large amounts of gases formed during the combustion reaction, Fig.9c. The flakes are composed of grains ranged from submicron to nanosize grains, Fig.9d. Characteristics faceted grains with nearly flat grain boundaries and 120º triple points indicate that in some extent the microstructure reaches the equilibrium. The fast thermal treatment during the synthesis combustion is responsible of such behavior.

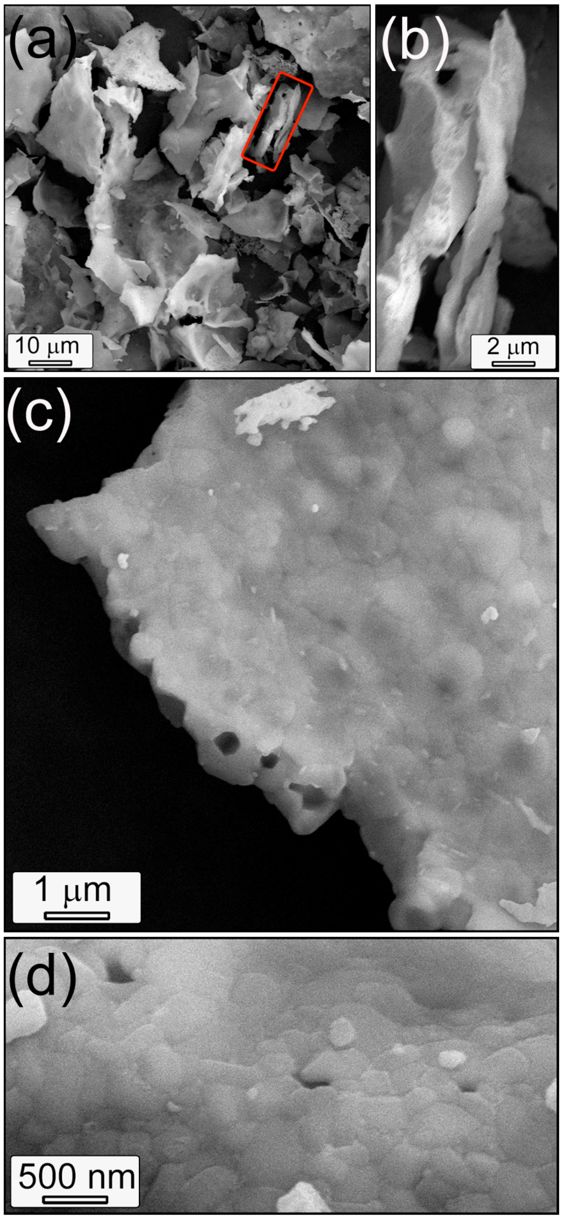

Figure 9. FESEM micrographs of nanostructured sheets of Sr$_{0, 97}$Al$_2$O$_4$: Eu$_{0, 02}$, day $_{0,01}$ powders obtained by the combustion method with urea content m=3 and an oxidizing agent.

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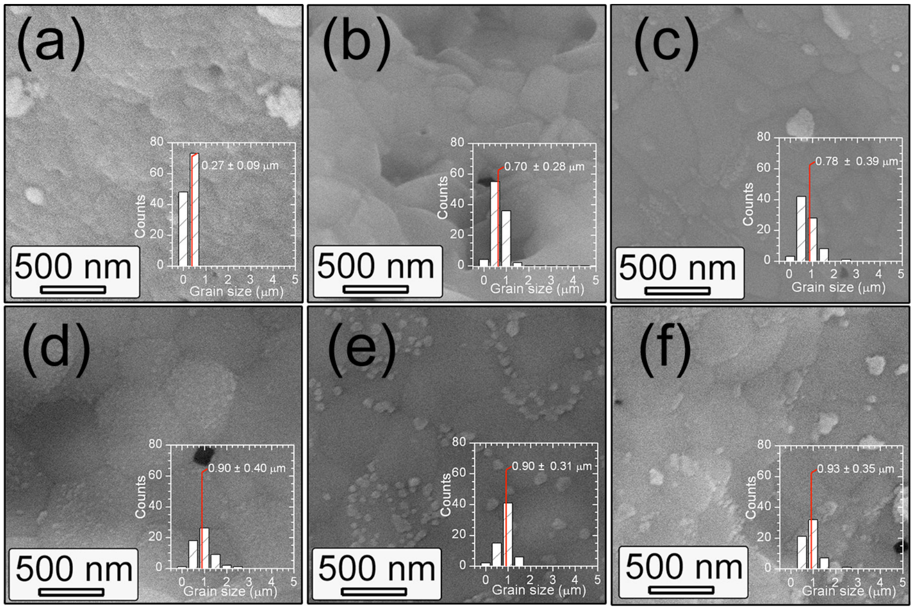

Figure 10. FESEM micrographs of powders obtained by combustion synthesis, including by using different urea content: **(a)** m=2; **(b)** m=2 after thermal treatment in Ar_2 at 600°C and **(c)** m=2 after thermal treatment in Ar_2 at 900°C; **(d)** m=3 with oxidizing agent; **(e)** m=4 with oxidizing agent; and **(f)** m=5 with oxidizing agents. Each micrograph show an inset with the grain diameter distribution in equivalent counts as measured from several FESEM micrographs.

The FESEM micrographs of the different combustion powder without oxidizing agent and urea content m=2 before and after thermal treatments are shown in Fig. 10a-c. FESEM micrographs of powders obtained by different amount of urea and adding oxidizing agent are shown in Fig.10d-f. Distribution plots of the grain sizes obtained by counting the grains and their equivalent diameter from the several micrographs. The average grain mean diameter and the standard deviation in each micrograph are given. The micrographs show the grain size of strontium aluminate based particles obtained by the combustion method grow with the post-synthesis temperature of the thermal treatment. The powder with m=2 possesses the lower grain size with an average value 0.27± 0.09 µm. An increase in the mean grain size with increasing temperature is observed, reaching values of 0.70± 0.28 µm and 0.78±0.39 µm after annealing at 600 °C for 2 h and 900ºC for 2h, respectively. The excess of urea plus oxidizing agent produce a higher grain size that denotes higher processing temperatures. For the different urea contents in presence of oxidizing agent, the average grain size reaches values ca. 0.90 µm. Fig. 5d, 5e and 5f show that the increase of urea creates cracks and there are small particles decorating the surface. Their nature is not being elucidated and could be associated with faster synthesis. There is a clear correlation between the larger grain size of the materials processed in the presence of the oxidizing agent. The higher temperature of processing produces larger crystallite size that account for superior luminescent response.

4. Conclusions

By combustion method avoiding thermal treatments in a reductive atmosphere the long afterglow $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors are successfully synthesized. The amount of urea has an important influence on the phase composition; urea contents larger than the stoichiometric one required the presence of an oxidant agent such as HNO_3 to complete the reaction.

The synthesized phosphor shows an intense band emission centered at 515 nm. The optical properties correlate with the crystallinity; higher crystallite size involves greater emission intensity. Highly crystalline particles having a flake type morphology are obtained. The combustion method avoids the standard requirements of post-thermal treatments in reducing atmosphere to promote the appearance of Eu^{2+} cations. A higher amount of urea in the presence of an oxidizing agent produces strontium aluminate particles with higher phosphorescence brightness due to the effective chelation of the cations and the creation of suitable atmospheric conditions to reduce the Eu^{3+} to Eu^{2+}. The luminescence properties correlate with the crystallite size of the strontium aluminate. Nanostructured particles with a thickness $\leq 1\mu m$ and persistent luminescence are considered as attractive material to use in applications that required low particle size and high phosphorescence. The optimized synthesis and processing conditions by the combustion method in presence of oxidizing agent provides micro-nanofunctional material with a larger after glow.

5. Acknowledgments

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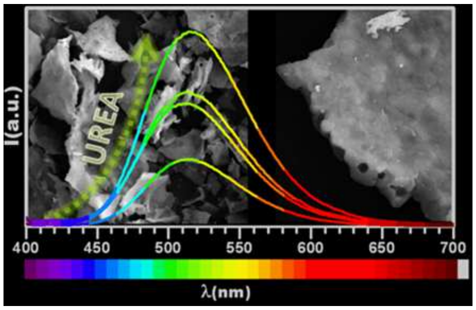
ToC figure



Well-controlled fuel/oxidizing agent ratio allows to synthesize Nanostructured Strontium Aluminates Lamellar particles with High Luminescence Properties

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