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SrAl₂O₄: Eu²⁺, Dy³⁺ doped-nanoparticles prepared by pulsed laser ablation in liquids

Hongli Du ^{a,b}, Victor Castaing ^a, Dongcai Guo ^b, Bruno Viana ^{a,*}

^a PSL Research University, CNRS, Institut de Recherche de Chimie Paris, UMR CNRS 8247
Chimie ParisTech, Paris, France

^b College of Chemistry and Chemical Engineering, Hunan University, Changsha, China

ABSTRACT

SrAl₂O₄: Eu²⁺, Dy³⁺ nanoparticles prepared by pulsed laser ablation in liquids (PLAL) could be a green and versatile technique to obtain inorganic nanoparticles with persistent luminescence and different morphologies and sizes. Laser ablation technique could deliver large amounts of energy highly concentrated into one point of a material and has been carried out in vacuum, in air and in liquids. Because of the unique confinement effect from liquid environment, there is many advantages when the laser ablation occurs in liquid. In this paper, we focus on the control of the size through proper laser parameters, choice of the reaction solution. Persistent luminescent SrAl₂O₄: Eu²⁺, Dy³⁺ phosphor was obtained by laser ablation in liquids.

Keywords: Laser ablation, nanoparticles, persistent luminescence,

1. INTRODUCTION

Pulsed laser ablation in liquids (PLAL) has demonstrated to be an efficient and versatile technique to produce high-quality nanoparticles of a wide range of materials¹. PLAL technique possesses a number of advantages. First, laser ablation process is considered as green chemistry process. Second, the nanomaterials with size dispersion below 100 nm can be produced in faster and cleaner ways, even if sometimes the compounds quantity is at a limited value. Third, as long as there is the related laser equipment, experimental set up is minimal, and chemical precursors are replaced by bulk materials obtained by solid state reaction, so PLAL could be considered as a low-cost method. Finally, PLAL can be used to construct some complex structure compounds or modify the surface of nanoparticles, such as, inorganic nanoparticles coated with organic molecules that can be obtained in one step, in-situ or ex-situ². Due to such advantages, the research on nanoparticles elaboration using PLAL has been of great interest during the last ten years. Nanoparticles obtained by PLAL methods, with size ranged between 5 and 100 nm, have been proposed for biological, optical devices or for photocatalytic applications. Laser ablation technique could deliver large amounts of energy highly concentrated into one point of a material, creating a localized plasma. The liquid environment could lower the heat load on the work piece, confines the vapor and plasma, and increases the shock pressure on the surface³⁻⁴. At the same time, the main fractions of the particles obtained by PLAL are often preserved with the same chemical composition as the bulk targets. This has been demonstrated with alloys⁵, and various oxides-based compounds⁶. Therefore, PLAL is generally considered to combine top-down (micro-sized solid targets) and bottom-up (the formed plasma, atoms and clusters) methods with major processes controlled by laser plasma and physical cavitation⁷. However, as other chemical synthesis processes, several parameters have to be optimized to get the highest possible quality of materials. In case of PLAL techniques, laser parameters (such as wavelength, pulse duration, laser energy) and the liquid environment (solvent, temperature, surfactant for instance) are the key points to optimize as reported in Table 1.

Table 1. Main laser parameters for PLAL

Main laser parameters	Size	Effect in yield and size distribution
Laser fluence	High effect	Larger NPs with increase laser fluence ⁸
Pulse duration	High effect	Increase of the size distribution with fs and ps lasers ⁹
Repetition rate	Small effect	Small increase of the size distribution with rep. rate ¹⁰
Laser wavelength	Effect	Higher yield for increase absorption ¹¹

With the increasing need of nanoparticles to be used in various applications, more and more researches focus on rare-earth doped nanoparticles. Rare-earth and transition metal doped nanoparticles present good photostability and wide possible optical features including the well-known up-conversion, down-conversion and persistent luminescence processes¹². Some of the researches on the lanthanide and transition metal activated nanoparticles prepared by PLAL have been summarized in Table 2. When the nanoparticles are prepared in liquid, special solutions or additives could protect the NPs from defects on the surface, improve the properties of nanoparticles and favor their good dispersion. Then, surfactant¹³ or inorganic additives¹⁴ are used to improve the crystallinity, morphology and to limit size dispersion.

Table 2. Lanthanide (top) and transition metal (bottom) doped nanoparticles prepared by PLAL technique

Materials	Size (nm)	Solution & surfactant	Shape
Rare earth doped NPs			
Y ₃ Al ₅ O ₁₂ :Ce ³⁺ ¹⁵	5-25	deionized water	Spherical
Y ₃ Al ₅ O ₁₂ (YAG:Ce) ¹⁶	9, 100	deionized water	String-like
Tb ₃ Al ₅ O ₁₂ :Ce ³⁺ ¹⁷		deionized water & lauryl dimethylaminoacetic acid betain (LDA)	
Y ₃ Al ₅ O ₁₂ :Ce ³⁺ (YAG:Ce)	2-5	deionized water & 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (MEEAA)	Nanorod
Y ₂ O ₃ :Eu ³⁺ , Gd ₂ O ₃ :Eu ³⁺		deionized water	
Y ₂ O ₃ :Eu ³⁺ , Lu ₂ O ₃ :Eu ³⁺ , Gd ₂ SiO ₅ :Ce ³⁺	5-10		
Lu ₃ TaO ₇ :Gd ³⁺ /Tb ³⁺ ¹⁸			
Sr ₂ MgSi ₂ O ₇ : Eu ²⁺ , Dy ³⁺ ¹⁴	/	deionized water + SiO ₂	Elliptical nanorod
Y ₂ O ₃ : Er ³⁺ , Yb ³⁺ ¹⁹	tens, hundred	deionized water	/
Ca ₂ Si ₅ N ₈ :Eu ²⁺ , Tm ³⁺ ²⁰	3.5	water & NaOH and acetate	Web-like
Ca- α -SiAlON:Eu ²⁺ ²¹	90-110	deionized water	Aggregation
CaMoO ₄ :Tm ³⁺ /Yb ³⁺ ²²	15-30	ethanol	Spherical
NaYF ₄ :Yb ³⁺ /Er ³⁺ ^{1, 23}	10-20;40-60	deionized water/ 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (MEEAA)	Spherical
YVO ₄ :Eu ³⁺ ^{6, 13, 24}	30-50	deionized water/sodium dodecyl sulfate	Ovoid-like
YOF: Er ³⁺ , Yb ³⁺ ²⁵	20-200	deionized water	Nanorod
NaGdF ₄ :Nd ³⁺ ²⁶	20-30	DMSO	Not completely spherical
Transition metal doped NPs			
ZnGa ₂ O ₄ :Cr ³⁺ ²⁷	130-400	water	Hexagonal prisms
ZnS:Mn ²⁺ ²⁸	7	water	Spherical
ZnS:Cu ²⁺ ²⁹	2.1-4	water	Quantum dots
[Ni _{1-x} Fe _x (OH) ₂](NO ₃) _y -(OH) _{x-y} nH ₂ O ³⁰	6.5 \pm 0.8; 13 \pm 1	water	Spherical

For the abundant applications of nanoparticles in various fields, such as, lighting, display, energy and biomedicine, it is necessary to obtain nanoparticles with high crystal quality, good morphology and uniform sizes. Lots of lanthanide-activated nanoparticles have been synthesized by PLAL, for instance, lanthanide-based down-conversion nanoparticles¹⁸ and up-conversion nanoparticles^{19, 23}. Concerning the persistent phosphors, the number of works is very limited. Recently, with transition metal cations, nano-sized deep red persistent luminescent materials (ZnGa₂O₄:Cr³⁺) were successfully prepared by the pulsed laser ablation in liquids without any surfactant²⁷. The nanoscale particles present excellent deep red long persistent luminescence that may be use in the future as new probe in the first biological window. Indeed, in our laboratory in Paris, we have demonstrated the strong interest for this matrix for bio-imaging applications by a pioneer work published in 2011³¹ followed by important breakthroughs in the field³²⁻⁴⁴. Based on the previous works, Ca₂Si₅N₈:Eu²⁺, Tm³⁺ is one pioneer nice example of the capability of PLAL technique to obtain RE doped NPs with persistent luminescence, and we further performed the first real-time *in vivo* imaging with Ca₂Si₅N₈:Eu²⁺, Tm³⁺ NPs obtained with PLAL method²⁰. PLAL elaborated Sr₂MgSi₂O₇: Eu²⁺, Dy³⁺ nano-phosphors can also present interesting persistent luminescence properties¹⁴. Following these pioneering works, the preparation of rare-earth doped persistent phosphors such as SrAl₂O₄: Eu²⁺, Dy³⁺ is encouraged through pulsed laser ablation in liquids.

2. MATERIAL SYNTHESIS AND EXPERIMENTAL PROCEDURES

SrAl_2O_4 : Eu^{2+} , Dy^{3+} compound, which is the most developed persistent phosphor due to its outstanding long afterglow time and intensity, has never been prepared by this technique. The persistent luminescence researches on this material began more than twenty years ago, with the discovery of SrAl_2O_4 doped with Eu^{2+} , then through co-doping with trivalent dysprosium, the afterglow was enhanced and reached more than 10 hours⁴⁵. Up to now, it is widely used in various identification and warning signs on buildings or highways. Furthermore, their high brightness and long-lasting time make this material interesting for further applications in biomedicine, the elaboration of NPs still remains a challenge⁴⁶, which propels to prepare nano-sized SrAl_2O_4 : Eu^{2+} , Dy^{3+} phosphor.

During the whole laser ablation in liquids, the nanoparticles formation process can be described as follows: when the pulsed laser irradiates the bulk target in liquids, breakdown process and plasma generation will take place. Then, because of the liquid environment, there will be a stronger confinement of the plasma and a fast energy transfer from the plasma to the surrounding liquid. Later, a cavitation bubble, which is a dynamic system with an expansion phase and a collapse phase, is formed. Finally, the cavitation bubbles will collapse when the bubble reaches its maximum radius⁷, and at the same time, NPs will be released in the liquid to form a stable colloidal solution. The following part describes the different steps.

The preparation of the SrAl_2O_4 : Eu^{2+} , Dy^{3+} persistent phosphor was realized through pulsed laser ablation in liquids under the following conditions. The sintered pellets are used as targets for preparation of SrAl_2O_4 : Eu^{2+} , Dy^{3+} nanophosphor. The experimental process to prepare pellets is introduced in Supporting Information. During the ablation process, the pellets are immersed in 50 mL of solution with a quartz cell, and irradiated with 1064 nm-pulsed Nd:YAG laser at 10 Hz (see Figure 1).

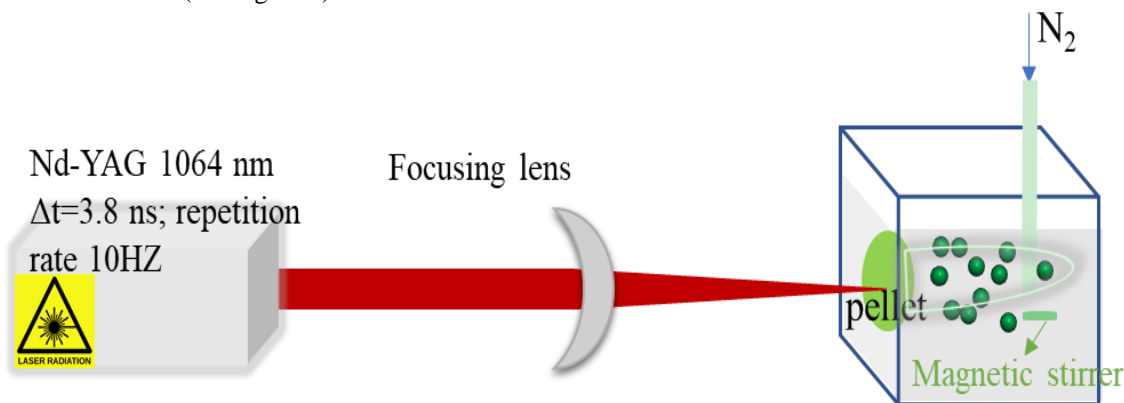


Figure 1. Schematic diagram of the PLAL experimental setup for SrAl_2O_4 : Eu^{2+} , Dy^{3+} synthesis

Different solutions such as water, ethanol, and acetone, different laser wavelengths (355 nm, 1064 nm) and different laser powers (10 mJ, 400 mJ) were used for the material preparation. First, with the laser ablation in water, it appears impossible to obtain the SrAl_2O_4 : Eu^{2+} , Dy^{3+} NPs but mainly SrCO_3 was formed¹⁴. This is due to the reaction between the Sr^{2+} ion and CO_2 dissolved in water. In order to remove the CO_2 from the solution, one should keep the process under Ar gas bubbling all along the synthesis. In ethanol and acetone solutions, as shown in Figure 2 presenting the XRD patterns, the obtained particles present SrAl_2O_4 phase. As already reported, SrAl_2O_4 has a tridymite structure constructed by corner sharing AlO_4 tetrahedra tilted with respect to each other⁴⁷. The occupation of Al^{3+} cations in the compound induced a charge deficiency that is compensated by Sr^{2+} cation incorporation in channels created within rings of corner shared AlO_4 tetrahedra, in the so-called stuffed tridymite structure⁴⁸. There are two possible positions for Sr^{2+} cations in this matrix.

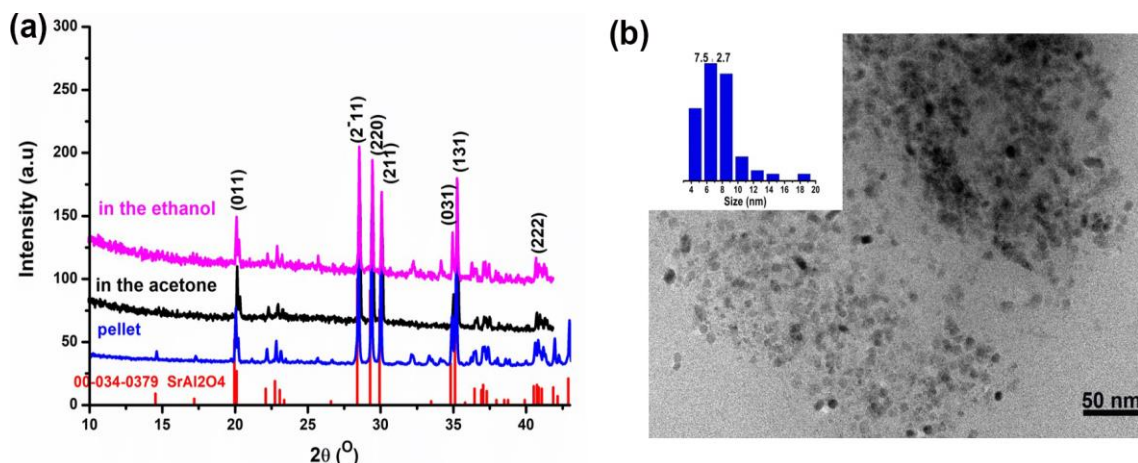


Figure 2. (a) XRD spectra of the synthesized particles in different solutions; (b) TEM of the nano-sized particles obtained in ethanol with 1064 nm

When laser energy value is fixed at 10 mJ, with the near-infrared wavelength (1064 nm), the yield of the obtained particles appears larger than that with the UV wavelength (355 nm). For the same wavelength (1064 nm), but with much higher energy (400 mJ), higher yield and larger particles are obtained. This can be explained by the pulsed laser ablation mechanism in the solution as presented before. During the pulsed laser ablation on the pellet, cavitation bubbles will be formed on the surface of the pellet continuously, and with laser power increase, the cavitation bubbles lifetime increases. As a result, this will enhance the quantity of particles formed during the laser pulse. At the same time, high laser power may cause mechanical stress, as the temperature and pressure inside the plasma plume are increased. This could further result in a collapse of the cavitation bubbles, which thereby intensify the collision frequency among particles, leading to coalescence and larger particles formation⁴⁹⁻⁵⁰. Considering large productivity and good crystalline phase, $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ NPs were prepared in either ethanol or acetone with laser wavelength at 1064 nm. Size distribution and optical feature also investigated are presented in the following part.

TEM image presents nanoparticles with sizes around 7.5 nm (see Figure 2.). As reported before, during the laser ablation process, particle size distributions could be composed of two modes. Small nanoparticles nucleate and grow in the target-solution mixing region based on thermal vaporization mechanism, while larger particles are formed by the fragmentation of the superheated molten metal layer attributed to explosive boiling mechanism⁵¹⁻⁵². The size distributions of the thermal modes for each laser condition are very similar, only second fragmentation mode appears to vary with laser parameters. The micro size particles are formed like a “top-down” method, while nano size particles are formed by the thermal nucleation in the cavitation bubbles.

3. OPTICAL CHARACTERIZATION

The photoluminescence spectra of the particles obtained by laser ablation in ethanol and acetone (laser wavelength 1064 nm) are presented in Figure 3. The typical emission spectra of $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ at 20 K with two emission bands located at 520 nm and 445 nm⁵³ are obtained for the laser ablation particles either in ethanol or acetone as shown in Figure 2. One could clearly observe an intensity variation between the two emission bands according to the elaboration medium.

The two crystallographically different sites for Sr^{2+} have different coordination numbers, similar average Sr-O distances (i.e., 2.695 Å and 2.667 Å respectively), but slightly different individual Sr-O distances. Indeed, the two environments differ by a slight distortion⁵⁴⁻⁵⁵. Considering the two slightly different Sr^{2+} sites, one can expect Eu^{2+} to occupy the sites more or less equally due to similar ionic radii. Non-radiative energy transfers between these two sites are proposed⁵⁶. Eu^{2+} cations in Sr II sites should present broad emission at higher energy (445 nm) while the Eu^{2+} in the Sr I sites should be responsible for the lower energy band (520 nm). Notice that there is only slight Sr-O distances variation between Sr-I and Sr-II.

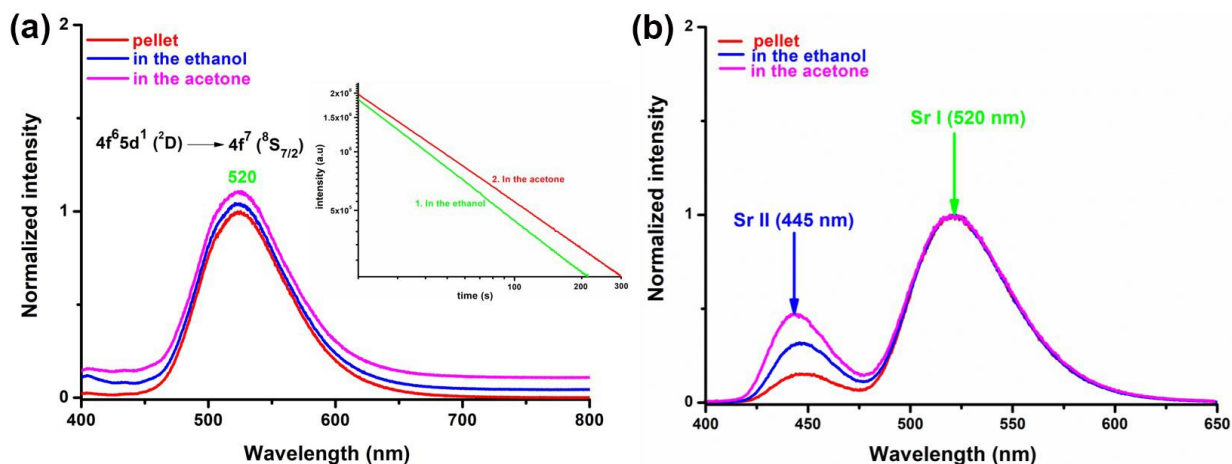


Figure 3. PL spectra of the synthesized materials at different temperatures. (a) at 300 K; (b) at 20 K. (Excitation wavelength at 365 nm, 10 Hz). Insert (a) is persistent decay curve of the ablated particles in acetone (1) and in ethanol (2) at 300 K, after being excited at 365 nm for 5 min.

In addition, at relatively high temperature, the energy can be transferred from Eu^{2+} in the Sr II site toward Eu^{2+} at the Sr I position, thus giving the redistribution of emission intensities from both sites at different temperatures^{47, 56}. This leads to a strong decrease of the 445 nm band in favor to the 520 nm emission, which corresponds to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ions in Sr I sites⁵⁷. The intensity at 445 nm of particles obtained in acetone is higher than that of pellet and particles obtained in ethanol, keeping the intensity at 520 nm constant, revealing different energy transfer efficiencies between the two sites according to the synthesis conditions. As Gökce et al. reported, through PLAL process, larger particles will be formed in ethanol in regard to acetone due to agglomeration happening in less polar solvents⁵⁸. Therefore, one can assume that the smaller particles obtained in acetone present larger energy transfer efficiency probably due to the variation of crystal field around the Eu^{2+} ion⁵⁹⁻⁶⁰.

$\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} bulk compounds present excellent long persistent luminescence, this phenomenon can be explained by the following processes. Firstly, under UV light excitation, Dy^{3+} stabilized electrons trapping and enhanced the persistent luminescence; secondly, the electrons could be slowly released at room temperature and recombined with the excited state of Eu^{2+} . Finally, when return to Eu^{2+} ground state, there gives rise to persistent luminescence⁴⁵. Figure 3-insert shows the persistent luminescence decay profiles of the ablated $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} NPs in acetone and ethanol. After excitation at 365 nm for 5 min at room temperature, the particles present persistent luminescence, but much shorter than that of their bulk counterpart compounds. Indeed, after about 5 min, the luminescence of the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} NPs is too weak to be seen by eyes. The main possible reason is probably related to the ultra-small size of particles and surface effects that occur in the non-optimized process, but also may be due to a reduction of the effective trap density as already reported⁶¹.

4. CONCLUSIONS

There are lots of materials successfully prepared by PLAL. In order to elaborate nanoparticles with limited size, good morphology and outstanding properties through PLAL technique, various laser parameters, multiple solutions, and many other factors have been investigated. However, due to the complex mutual-effects between these parameters, it is difficult to develop a single standard, especially for the bimodal sized nanoparticles' formation by PLAL, even if some experimental devices, such as filters, are known to help controlling the particles size. In addition, upscaling of the quantitative yield of nanoparticles is another issue that still need to be solved.

In the present work, we succeeded to synthesize $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} NPs with PLAL. But at this time, the control of the uniform nano-size remains difficult while the intensity of the persistent luminescence is far from those obtained in the micro size compounds. In the following steps, one should further better control the laser parameters and use various additives in the solution to enhance the optical properties. In case of success, this should open the path to new applications and new modality as bio-label or in catalysis applications for instance.

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