

Microwave Synthesis of a Long-Lasting Phosphor

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The best way to get a student interested in learning science is to provide insights into high-technology materials with impressive properties. The “Chimie: Science Magique” program was created at this university to develop high-impact laboratory experiments for undergraduate students to synthesize and use appealing materials with “magical” properties. However, many high-tech materials syntheses need complex equipment and advanced experimental skills. In this article, we describe the synthesis of long-lasting phosphors and demonstrate both their fluorescent and phosphorescent properties. This experiment only requires basic experimental skills and limited equipment.

The synthesis of strontium aluminates, SrAl_2O_4 , doped with europium and dysprosium, $\text{SrAl}_2\text{O}_4:\text{Eu}:\text{Dy}$, gives students insight into solid-state synthesis by a combination of self-propagating combustion and microwave methods; doping; photochemistry; microscopic structure of solid-state; and rare earth chemistry. These experiments were carried out by first- and second-year undergraduate students. The study of phosphors was relevant to the introduction of condensed matter chemistry.

Long-lasting phosphors are materials that can store energy under light exposure and then release this energy, glowing in the dark for some time. They are part of our everyday life on the hands of our watches, security signs, and in glow-in-the-dark toys. In recent years, there has been an increasing need for efficient long-lasting luminescent materials. During the past decades, the only commercial phosphorescent material was Cu (or Co)-doped zinc sulfide (ZnS) (1), but these materials could only glow for tens of minutes and were sensitive to moisture. The only alternative materials were phosphors containing radioactive ions such as promethium (Pm^{3+}), where the β -radiation coming from the disintegration of Pm ions is converted into visible light. Nevertheless, the radioactivity of such materials makes them a potential environmental hazard.

In the mid-1990s, a new family of phosphors was discovered: a strontium aluminate doped with lanthanide atoms (europium and dysprosium) as co-activators, $\text{SrAl}_2\text{O}_4:\text{Eu}:\text{Dy}$ (2). This new phosphor glows for tens of hours, is chemically inert, and considered non toxic (3). This material is efficient enough to be used in security signs (guidance systems to emergency exit, emergency signaling, and so forth). It does not require a battery to glow and is charged by a brief exposure to day light.

The usual synthesis of strontium aluminates uses stoichiometric amounts of oxides or carbonates of the constituting metals, heated for 24 hours at 1300 °C under a reductive carbon atmosphere (4). At this temperature, a solid-state diffusion of the different atoms occurs and the aluminate is formed. Such high temperature conditions over this time scale are difficult to achieve in a student laboratory as the most common lab ovens cannot reach such a temperature, particularly under a controlled atmosphere. Other methods using sol-gel (5), self-propagating combustion, or microwave synthesis have been also proposed (6, 7), but are still far too time consuming and complex to be

implemented in an undergraduate laboratory. We prefer a new approach using a combustion synthesis somewhat similar to the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ synthesis (8) but replacing the high-temperature furnace by a microwave oven that gives better control over the experimental conditions. This new method, allows the synthesis of $\text{SrAl}_2\text{O}_4:\text{Eu}:\text{Dy}$ in less than four minutes by using microwaves and self-propagating combustion techniques starting from metal nitrates and urea as a fuel.

The doped SrAl_2O_4 from the new method shows fluorescence (green) and a long-lived phosphorescence (a few hours) after exposure to a UV lamp in a dark room. The full synthesis of this long-lasting phosphor could readily be achieved in a one-hour session. Some variation could be used in the synthesis to underline the effect of the crystal field on the phosphor color by changing Sr for Ca atoms. The doping level could also be investigated by either changing the total rare earth quantity or the Eu/Dy ratio.

These experiments are easy to perform and could be demonstrated at the high school level.

Materials and Methods

Students are given beakers, evaporating dishes, spatulas, a watchglass, a Buchner funnel, a sidearm flask, filters, tongs, crucibles, gloves, goggles, strontium nitrate, aluminum nitrate, europium nitrate, dysprosium nitrate, and urea. They are supplied with distilled water as the solvent and technical ethanol as a washing solution. They have access to precision weighing balances, a 950 W microwave oven (under a fume hood and behind a hood window), and a drying oven.

The material is synthesized from a solution of the different metal nitrates by dissolving 11 mg of europium nitrate, $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$; 23 mg of dysprosium nitrate, $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$; 1688 mg of aluminum nitrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; and 513 mg of strontium nitrate, $\text{Sr}(\text{NO}_3)_2$ in a small volume of deionized water (20 mL) in a 250 mL beaker. All the nitrates can be mixed without danger, but *no urea* should be added before all the nitrates powders are completely dissolved: the nitrate–urea solids mixture is potentially explosive. Then, 3.8 g of urea (NH_2CONH_2) is added to the solution and stirred until the urea is completely dissolved. The solution is covered with a thick watchglass and placed in a microwave oven at 950 W for 3.5 minutes. The microwave oven was located in a fume hood behind a closed window as some nitrogen oxides can be formed during the reaction. After the 3.5 minutes, the microwave door is opened, the hot watchglass is removed using tongs and the beaker (*still very hot*) is allowed to cool down to room temperature.

A white–yellowish powder that shows a green–blue fluorescence under UV light (standard, $\lambda = 365$ nm, power = 8 W) exposure is obtained. The powder is crushed and washed using the Buchner funnel and the sidearm flask under vacuum with both distilled water and ethanol. Then the solid is dried at 100 °C in a drying oven. The resulting white powder (Figure 1A) can be

tested for fluorescence and phosphorescence under UV light. A strong green fluorescence (Figure 1B) and long-lived time green phosphorescence are observed (Figure 1C).

It should be noted that both fluorescence and extremely weak phosphorescence (on the order of a few seconds) are also observed for the *undoped* SrAl_2O_4 sample (certainly due to the presence of defects) (Figure 1D). This compound can be synthesized without expensive lanthanide chemicals at a high school level.

The students can vary the experimental conditions by changing the Eu/Dy ratio or the Sr/Eu ratio, which leads naturally to the introduction of theoretical subjects such as the spectra of lanthanides or the quenching effect for high rare earth content. It is also possible to investigate the effect of urea. If the urea mass is decreased to 413 mg, the powder obtained is a red phosphor under UV light without any observable phosphorescence (Figure 1H).

The synthesis was adapted to produce $\text{CaAl}_2\text{O}_4\text{:Eu:Dy}$ (Figure 1E), by replacing the strontium nitrate by 572 mg of calcium nitrate tetrahydrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and heating for 3 min in the microwave oven. The doped aluminate displays a blue fluorescence (Figure 1F) and blue phosphorescence (Figure 1G).

Hazards

The strontium, calcium, and aluminum nitrate are only weakly toxic (irritant and harmful if swallowed). The toxicity of the Eu and Dy nitrates is also considered moderate (irritant and harmful if swallowed) even though they have not been fully investigated.

As the nitrate compounds are strong oxidizers they should never be mixed directly in the solid state with a reducing agent such as urea because of the risk of fire or explosion. *Urea should always be added after full dissolution of the solid nitrate in water.* The total amount of reactants used should be changed with the greatest care as it could increase the quantity of heat released, which could damage the material. No uncontrolled reaction has ever occurred with the proportions used, but hot yellow flames can sometimes appear as the reaction occurs. No sealed or narrow-neck container should be used as large quantities of gas are produced during the reaction. As a precaution, no student should be allowed to stay too close to the microwave oven during the reaction, and a shield or a hood window should be used as another protective barrier between the students and the microwave oven. We also strongly advise the use of a microwave oven specifically designed for the laboratory to handle chemical reactions. During the microwave combustion, some nitrogen oxides are produced and the microwave oven should remain in a hood. UV light irradiations are potentially harmful to the retina and to the skin, no student should directly look at the UV light and skin should be covered. Wearing anti-UV coated goggle is strongly advised. The produced phosphors are described as weakly toxic or non-toxic, chemically inert, without any particular caution for storage.

Results and Discussion

Crystallographic Structure of the $\text{SrAl}_2\text{O}_4\text{:Eu:Dy}$ and $\text{CaAl}_2\text{O}_4\text{:Eu:Dy}$ Phosphors

The strontium aluminate SrAl_2O_4 has a tridymite structure (9) (Figure 2A) associated with a monoclinic unit cell. In this structure, Al atoms form tetrahedral AlO_4 units creating chan-

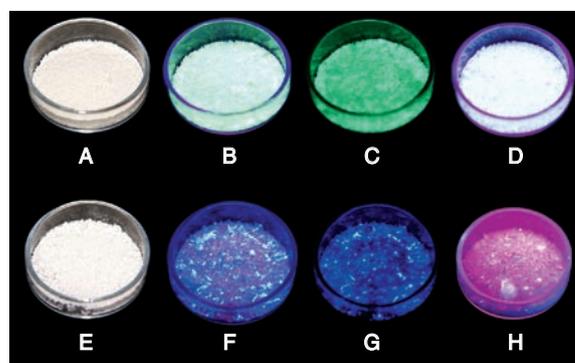


Figure 1. $\text{SrAl}_2\text{O}_4\text{:Eu:Dy}$, formed after the microwave combustion method, in sunlight (A) and with UV light exposure: green fluorescence (B), and after UV light exposure, in the dark: green phosphorescence (C). Undoped SrAl_2O_4 with UV light (D). $\text{CaAl}_2\text{O}_4\text{:Eu:Sr}$ in sunlight (E), with UV light exposure: blue fluorescence (F), and after UV light exposure, in the dark: blue phosphorescence (G). $\text{SrAl}_2\text{O}_4\text{:Eu:Sr}$, low-urea content, with UV light exposure: red fluorescence (H). The colored version is available in the table of contents and in the online PDF.

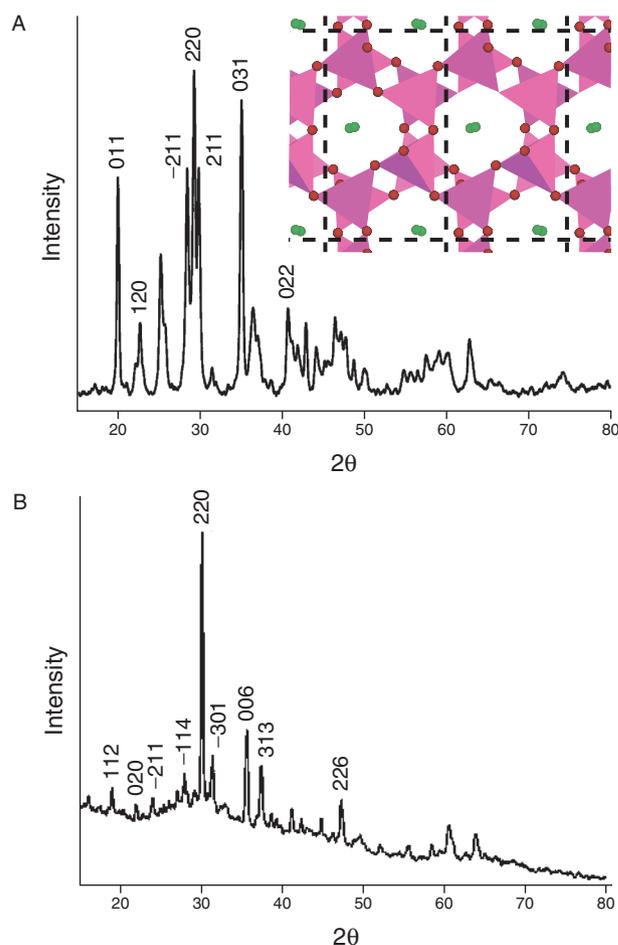
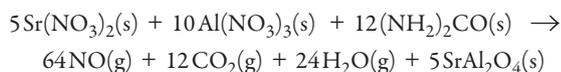


Figure 2. Powder XRD spectrum of (A) SrAl_2O_4 and (B) Eu/Dy co-doped CaAl_2O_4 , using $\text{Cu K}\alpha$: only the main reflections are indexed (JCPDS 34-379 and 70-0134, respectively). Inset in A: Stuffed tridymite structure of the SrAl_2O_4 : oxygen atoms (dark-colored balls) are at the vertices of the tetrahedra; aluminium atoms are at the center of the tetrahedral (light-colored balls); strontium atoms are located at the center of the channels (light-colored balls). The dashed lines show the unit cell.

nels where Sr atoms are located. The Eu^{2+} or Dy^{3+} dopants substitute the Sr^{2+} atoms as they have a similar ionic radius. The X-ray diffraction (XRD) pattern of $\text{SrAl}_2\text{O}_4\text{:Eu:Dy}$ is very similar to that of pure SrAl_2O_4 , except for some peaks corresponding to alumina and strontium carbonate by-products (not shown). The XRD pattern of $\text{CaAl}_2\text{O}_4\text{:Eu:Dy}$ is given in Figure 2B.

The Self-Propagating Combustion Method

We describe a self-propagating combustion method. Rather than using the high temperature of a furnace, we take advantage of the strongly exothermic reaction of nitrates with an organic fuel (urea) to locally induce an extreme temperature to form the ceramic. The metal nitrates are dissolved in water together with urea to homogeneously disperse the ions in solution. This process maximizes the atomic mixing, contrary to the high-temperature synthesis where the products are not mixed at the microscopic scale. Usually the water is boiled using either a low-temperature furnace (at $600\text{ }^\circ\text{C}$) or microwave oven until the flashpoint, inducing a high temperature reaction (beyond $1500\text{ }^\circ\text{C}$). The following is the assumed equation for this reaction:



The reaction releases enough energy to self-propagate for a few seconds until all the reagents are consumed and the desired product formed.

In this lab experiment, we use a microwave oven that works as well or even better than a furnace. In a single step, the solvent is evaporated and the self-propagating reaction is ignited because heavy atoms such as Sr strongly absorb microwaves. Moreover, this process allows the control of the oxidative reaction conditions. The stoichiometric reaction could be violent creating a high temperature yellow flame that induces the oxidation of Eu^{2+} to Eu^{3+} in air. The resulting strontium aluminate displayed a red fluorescence but without any long-lasting behavior. Thus a 10-fold excess of urea is used as reducing reagent to prevent reoxidation of Eu^{2+} by dioxygen during the reaction and the cooling step.

This process allows the production of high quality ceramics in a short time. The crystallinity of SrAl_2O_4 is not modified by an excess of urea. Nevertheless, the purity could be enhanced by washing. A small mass of boric acid (30 mg) can be added if needed to decrease the crystallographic defaults and thus enhance the luminescence properties (10).

Fluorescence and Phosphorescence

The electronic structure of a strontium aluminate or calcium aluminate compound resembles that of a typical insulator with a filled valence band (VB) and an empty conduction band (CB) (Figure 3) (11). The irradiation with photons of energy greater than the band gap (the minimum energy to excite an electron from the VB into the CB) creates an excited state with an electron in the CB and a hole (of electron) in the VB. Both electron and hole are still linked together by electrostatic forces (as they are oppositely charged) forming a pseudo-particle called an exciton. The recombination of the electron and the hole produces a UV photon (i.e., not in the visible region). To make SrAl_2O_4 emit visible light, a well-chosen lanthanide has to be added (Eu^{2+} in this case). Adding Eu ions creates an electronic level in the band gap (Figure 3, left). When the electron-hole pair (exciton) is created with light exposure, it can be trapped by the mid-gap level (Figure 3, left, 3); the excess energy being converted to heat. When the electron in this trap and a hole recombine, the energy can be transferred to the f electrons of the Eu atoms. As the f electrons in lanthanide rare earths are mostly located in the inner shell, the light emitted is weakly dependent on the Eu^{2+} environment and leads to a blue-green light emission. Depending on the chosen alkali metal the emitted light can be tuned from green (Sr) to blue (Ca).

The emitted photon has a longer wavelength than the absorbed photon: the sample can be irradiated by UV light ($\lambda \sim 365\text{ nm}$) and emits a green visible light ($\lambda \sim 500\text{ nm}$), demonstrating the fluorescence (see Figure 1B). When the UV light is turned off, the greenish emission takes some time to disappear hinting that the electron-hole recombination is a slow process. This experiment demonstrates the phenomenon of phosphorescence, which is the root cause of the glow-in-the-dark materials (see Figure 1C).

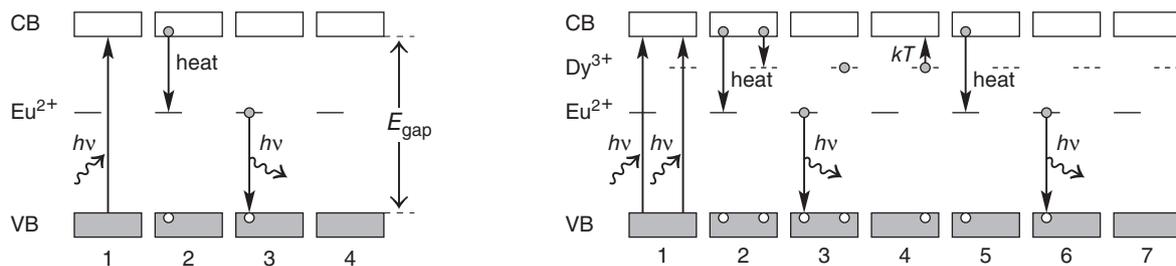


Figure 3. Simplified mechanism for phosphorescence of $\text{SrAl}_2\text{O}_4\text{:Eu}$ (left) and of $\text{SrAl}_2\text{O}_4\text{:Eu:Dy}$ (right). The Eu^{2+} level is a solid line and the Dy^{3+} level is a dashed line. The filled valence band is labelled VB and the empty conduction band CB.

Left: (1) Creation of a hole–electron pair by UV irradiation. (2) Trapping of the electron–hole pair by an Eu defect and heat release. (3) De-excitation of the trapped electron–hole pair and emission of a green light photon. (4) Unexcited material.

Right: (1) Creation of hole–electron pairs by UV irradiation. (2) Trapping of electron–hole pairs by Eu and Dy defects and heat release. (3) De-excitation of the Eu trapped electron–hole and emission of green light photon. (4) The Dy trapped electron–hole pair is thermally released into the conduction band. (5) The electron–hole is trapped by the Eu defect. (6) De-excitation of the Eu trapped electron–hole and emission of another green light photon. (7) Unexcited material.

Once all the Eu-trapped electrons have recombined, no more light can be emitted. To increase the efficiency, a so-called “activator” is added (see the right side of Figure 3). In our case, dysprosium ions (Dy^{3+}) add new shallow (electron) levels in the SrAl_2O_4 band gap just below the CB. These levels can trap electrons under illumination. When the electrons in the Eu traps have been used to produce light, the Dy-trapped electrons are then trapped by the Eu dopant and produce more light while recombining. The Dy activator allows storing more energy during the initial illumination, enhancing the long-lasting properties of SrAl_2O_4 .

We performed spectroscopic analysis on the low-urea red fluorescent material and on the green phosphorescent materials to confirm the origin of the radiative emission observed for these materials. This experiment is not necessary for the comprehension of the phenomenon and need not be carried out by the students. Moreover, spectrofluorimeters are not widely available in students labs. The excitation light was a xenon lamp with a monochromator. The samples were pressed as pellets and the emitted light was collected in reflection geometry. The materials were excited with photons in the same energy range as previously done with a basic UV lamp (Figure 4). The low-urea condition $\text{SrAl}_2\text{O}_4\text{:Eu:Dy}$ displays the typical spectrum of Eu^{3+} in an oxide matrix when excited at $\lambda = 395$ nm, while the high-urea condition leads to a wide band suggesting the luminescence of co-activated $\text{SrAl}_2\text{O}_4\text{:Eu:Dy}$. The quantum efficiency could not be measured accurately on an absolute range. The phosphorescence light can be observed, in full dark, after more than 5 hours following the initial light exposure: a complete study of time decay for a commercial phosphor has already been described (12).

Conclusion

This laboratory experiment allows the student to learn about solid-state synthesis, phosphorescence, and fluorescence. The experimental skills are basic (weighing, mixing). The materials show strong “glow-in-the-dark” properties that arouse a broad interest from the students. Modification of the synthesis to improve the material properties can also be performed as an introduction to a material science or engineering course. The experiments are also appropriate for high school chemistry, undergraduate chemistry, or materials science laboratory courses.

Acknowledgments

This solid-state synthesis was developed and optimized for the “Chimie: Sciences Magiques” program and sponsored by the Université Montpellier 2. The authors are grateful to Robert Crabtree and Odile Eisenstein for their patient reading of the manuscript.

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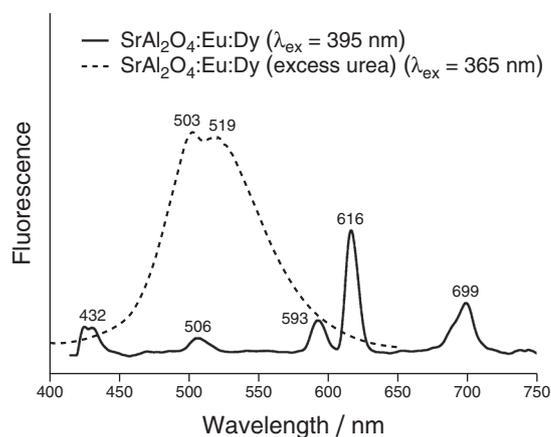


Figure 4. Fluorescence spectra of low-urea content red fluorescent (solid line) and higher-urea content green phosphorescent $\text{SrAl}_2\text{O}_4\text{:Eu:Dy}$ (dashed line).

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