MECHANISM FOR LONG PERSISTENT PHOSPHORESCENCE IN $\text{Sr}_2\text{MgSi}_2\text{O}_7$:Eu$^{2+}$

by

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(Under the direction of Uwe Happek)

ABSTRACT

In this thesis I will discuss the historical research on the phosphor material $\text{SrAl}_2\text{O}_4$:Eu$^{2+}$, as well as $\text{Sr}_2\text{MgSi}_2\text{O}_7$:Eu$^{2+}$. Both of these phosphors are possible replacements for the first generation green phosphor materials. I will also discuss my own research on these phosphors, as well as propose a new mechanism for the long persistent phosphorescence seen in these materials.

INDEX WORDS: phosphor, luminescence, Strontium, aluminate, magnesium, silicate, rare earth
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by

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1.1 **Luminescence and Phosphor Materials**

As an observed phenomena luminescence has been around since ancient times. Many organisms and some biological processes can generate their own emissions. Since the late 1500’s this ”weak glow” [1], literally translated from the original Latin, has been a popular field for scientific research. However, it took until 1852 for a law of luminescence to be derived. This first law is Stoke’s rule, which states that the emission wavelength from a luminescent material is always greater than the absorption wavelength that generates it. This emission was not given a name until the end of the 1800’s when Wiedemann first introduced the term in 1888. Wiedemann was also the first person to try to develop a scientific definition of luminescence. He stated that luminescence was the emitted light produced by a material that exceeds the light generated by the thermal background. This definition includes the most important property of luminescence, however, it is not enough to distinguish it from other forms of common emission. This definition does not even exclude reflection and refraction, nor does it exclude Raleigh and Raman scattering or Cherenkov radiation. Therefore in 1951 Vavilov proposed that the definition be amended to require the duration of the light emitted to be of much greater length than the period of light oscillations producing it.

It is not surprising that phosphors have almost an identical definition. In fact, phosphors are materials that are luminescent. As such Blasse defines a phosphor as ”... a solid which converts certain types of energy into electromagnetic radiation over
and above thermal radiation."[2] This definition excludes electromagnetic emission
due to black body radiation. These emissions from phosphors are usually constrained
in the visible spectrum, though this is not universally true. We can differentiate phos-
phors depending on the type of energy that they absorb: this energy can come from
electric voltages giving us electroluminescence, chemical reactions giving us chemilu-
minescence, X-rays, leading to X-ray luminescence, through photons for photolumi-
nescence. This last method will be the type of phosphors discussed in this paper.

In general the schematic for a luminescent material is quite simple. Imagine the
material as having two distinct energy levels. At some initial time an electron is
located in the lowest energy level $E = 0$. This electron is then excited using whatever
energy source is necessary. The electron is excited into a second, higher energy site.
The electron will then release this stored energy as a photon as it relaxes back into
the ground state. If this emission of electromagnetic radiation were the only method
of relaxation for this electron it would be correctly concluded that every material
is therefore a phosphor. Of course this is not the case, as there are competing pro-
cesses that allow the electron to relax back to the low energy site. These processes are
grouped together in a rather broad category called simply non-radiative processes.
The most common type of non-radiative decay is through vibrational energy. In this
way the absorbed energy of the electron is used to excite the host lattice. This exci-
tation is lost as thermal heat.

The majority of luminescent materials comprises activator ions, or luminescent
centers, trapped in a host lattice. The most famous of these materials is ruby. Ruby
is a crystal comprised of a host lattice of aluminate or Al$_2$O$_3$, with a Cr$^{3+}$ activator
ion. For the case of ruby, the activator ion is the only component that contributes to
the emission. The Cr$^{3+}$ ion absorbs UV as well as visible light, and then emits a deep
red luminescence.
There are two characteristics of luminous materials that are easily measurable. The first of these is the excitation spectrum of the phosphor. This is simply a measure of the photon wavelengths absorbed by the phosphor which cause luminescence. This spectrum usually matches that of the absorption spectra of the phosphor. The second important measurement we can preform is to measure the emission spectra. In this case the wavelengths of the light emitted from the phosphor are measured after the sample has been energized. There are two other measurable quantities worth mentioning here, the first is the radiative lifetime, while the second is the non-radiative lifetime. These will be discussed in more detail later in this thesis. The luminescent process for many materials can be more complicated than this simple case.

In many phosphors one or more energy transfer processes occur. The excitation photon is not absorbed by the luminescent ion, but is absorbed by what is called a sensitizing ion. Here the sensitizing ion absorbs the light quanta, which promotes an electron to a higher energy level. This electron non-radiatively relaxes back down to its lower energy level. The energy from this relaxation is transferred to an electron in the luminescent ion. This electron is then be promoted to its higher energy level, and when it relaxes to the ground state it releases the energy as a photon.

In some cases the sensitizer ion is not needed to create an energy transfer process. In fact if we use a high enough energy source to excite our crystal, like X-ray radiation, we can actually excite the host lattice producing lattice vibrations. The energy absorbed by the crystal is transferred to the optical impurity ion, producing the emission spectra of our impurity. In the case of yttrium vanadate doped with europium ions or, \( \text{YVO}_4: \text{Eu}^{3+} \), we can excite the vanadate, or host lattice with, UV light. However when we record the emission spectrum of this material we see only the spectra of the europium emission. This tells us that the host lattice transfers its energy to the luminescent material.
Finally there is a distinction to be drawn between luminescence and phosphorescence. All that has been discussed so far is consider luminescence. For phosphorescence we again start with an electron in its ground state energy level. The electron is again promoted to a higher energy level by an incoming photon. The electron then ”moves” to a secondary site. This site is called a trap and will hold the electron for some time. Eventually the electron is released from this trapping site, where it moves back to the luminescent ion. The electron then relaxes to the ground state, releasing an emission photon.

1.2 Applications of Luminescent Materials

One of the most important applications of photoluminescent materials are fluorescent lamps, which dates back to before the second world war. Fluorescent lamps are made from a long glass tube. This tube is filled with mercury gas. Mercury has a very specific emission of around 254 nm when a current is passed through the gas. This puts the mercury emission peak in the UV which is outside of the range of the human eye. In order to make this emission useful, a group of phosphors are coated on the inside of the glass tube. When these phosphors are excited by the mercury discharge they emit visible light. The phosphors and the ratios of their presence are chosen to exactly match the human eye’s color receptors in order to make fluorescent lighting appear as white light.

With the addition of rare-earth ions to the phosphors used in fluorescent lighting huge strides have been made in the color rendering of fluorescent bulbs. This has allowed the sale of these bulbs to move from the industrial and commercial sector, to regular household use as well. With the addition of ions such as divalent europium, and trivalent gadolinium, terbium, cerium, and others, we can fool the eye in to believing it is seeing the same light spectra that is produced by the Sun. Another important use for phosphor material is the cathode ray tube. Even though the current development
of liquid crystal displays, and plasma screen monitors, is diminishing the use of the cathode ray tube it is still an important device in many households. The cathode ray tube is made from a thick piece of glass and an electron “gun”. The glass is coated on the inner surface with a visible light emitting phosphor. For a color television, or monitor, there are three electron guns which can bombard the different phosphors on the screen. Each gun excites a specific phosphor causing it to emit a photon of a specific color. By scanning the electron guns across the screen, and pulsing the electron beam the image on the screen is produced.

Another use for luminescent materials is in the field of radiation detection. With the increased threat of the use of weapons of mass destruction, in particular the fear of a smuggled in “dirty” bomb, or a standard nuclear weapon, a method for quickly detecting their characteristic radiation is needed. One approach to this problem has been to try and develop a “fast” acting scintillator material. A scintillator is a material that can absorb the α and γ particle radiation emitted by radioactive isotopes and then emit a visible photon. Scintillators are usually made of large single crystals and plastics. Scintillators can be used not only as a security monitor, but they are also useful in the medical field as well. They can be used as receptors for a PET, or positron emission topography, scan and in CAT, or computer assisted topography scan.

Another main use for luminescent materials is as a lasing material. The very first solid state laser used ruby, Al₂O₃:Cr³⁺, as its active medium. In order to produce a laser the electrons from an emission source must be held in their excited state. This creates a population inversion in the energy levels. Eventually one of these excited electrons will return to its ground state. This stimulates other electrons to release a photon and return to their ground state. This stimulated emission is monochromatic, non-divergent, and coherent.

A final type of use for phosphors, and in particular for persistent, or long lived phosphors, is for ”glow in the dark” materials. These materials have uses in personal
safety devices, as emergency lighting devices, in golf balls and frisbees that can be seen at night, to emergency release handles on the inside of automobile trunks, and in emergency exit labels in buildings. The use of these long persistent phosphors are widespread and increasing constantly.
Chapter 2

Persistent Luminescence

2.1 Early Phosphors

One of the first, and most widely used long persistent phosphors on the market was zinc sulfide doped with copper. This phosphor has a green emission of around 530 nm, which is very well suited to the response of the human eye. Unfortunately, this peak emission is not particularly bright, and the persistence is on the order of a few hours limiting its use in applications requiring a visible signal to be observable overnight, i.e. in emergency exit signs, and even in clocks, and watches. In order to increase its use in these applications the perceivable emission from the phosphor had to be extended. An overall increase in the emission brightness was needed as well. By adding certain radioactive isotopes both conditions were met. The most widely used isotope was tritium, (H-3). This can cause health and safety issues, and therefore people have searched for a long persistent phosphor free of such isotopes.

In the 1960’s and 1970’s researchers began to experiment with strontium aluminate doped with europium or SrAl₂O₄:Eu²⁺. This phosphor was known to give a strong green luminescence in the region of about 520 nm. It was used mostly in cathode ray tubes as the green phosphor, but work done by Palilla et al. [3] showed that the sample had a long phosphorescence after a short bright decay. Since the addition of other rare earth ions had been known to increase the luminescent lifetime of other phosphors, Matsuzawa et al. attempted to use this to increase the long luminescent lifetime of SrAl₂O₄:Eu²⁺. They produced SrAl₂O₄:Eu²⁺,Dy³⁺ which is both extremely bright, and has a long luminescent lifetime of greater than ten hours.[4]
Chapter 3

Long Persistence Mechanism Debate

In 1968 Frank C. Palilla began to research the effect of divalent europium added to alkaline earth aluminates. In particular he focussed on SrAl$_2$O$_4$:Eu. He found that this crystal showed outstanding responses to both long and short UV excitation, as well as decent response to cathode rays. The sample produced made a very good replacement for Zn$_2$SiO$_4$:Mn, which was the commercial phosphor in fluorescent lighting at the time. In figure 3.1 we can see the excitation curve, while 3.2 shows the emission curve for the SrAl$_2$O$_4$:Eu$^{2+}$ produced by Palilla et al [3]. Notice that the emission peak for the sample, is centered around 520 nm making this crystal almost perfect as a green phosphor for the lighting industry.

Victor Abbruscato then went on to determine the trapping mechanism for this phosphor. In particular he wanted to find if the electrons or holes were trapped. Victor Abbruscato measured the Hall effect of the strontium aluminate sample using ultraviolet excitation. He claimed that his results showed that the charge carriers are the holes, and not the electrons. Since his experiment was conducted on a sample of strontium aluminate that was produced with an excess of alumina, Abbruscato claimed that this excess alumina produced an unknown defect site in the host crystal lattice. "This defect has the property of being a hole donor, as was shown by the Hall measurement." [5] He then associated this lattice defect site with the doped europium. He concluded this because the absorption bands are not seen in the strontium aluminate host before europium doping.
Figure 3.1: This shows the excitation spectra of SrAl$_2$O$_4$:Eu taken from [3].
Figure 3.2: The emission spectra of the SrAl$_2$O$_4$:Eu sample taken from [3]. This shows the relative energy plotted versus the wavelength.
By analyzing the emission curves, Abbruscato determined that the hole trapping levels depend on the amount of alumina added while producing the sample. The amount of traps appear to be directly related to the concentration of the alumina used. The excess alumina can be incorporated in two different methods. The first is that the excess alumina is incorporated interstitially. The second option is that the alumina can force a Sr\textsuperscript{2+} vacancy. Abbruscato concluded that the latter method is the correct one, as this method will allow for easier oxidation of the europium ions from Eu\textsuperscript{2+} to Eu\textsuperscript{3+}.

Another possibility proposed, and tested by Abbruscato, is that the Eu\textsuperscript{2+} acts as the hole trapping mechanism. This method was eliminated by producing a high alumina sample. This sample is then held at liquid nitrogen temperatures and irradiated with UV light for an hour. The emission spectrum of the sample was then taken with 325 nm excitation. This emission spectra showed no lines at 600nm or 625nm, which would directly correspond to the emission of Eu\textsuperscript{3+} we should see these emissions in the SrAl\textsubscript{2}O\textsubscript{4}. Therefore it can be concluded that Eu\textsuperscript{2+} is not the hole trapping agent.

In 1996 Matsuzawa et. al. proposed a modified phosphor with increased brightness. This group added trivalent dysprosium to the standard SrAl\textsubscript{2}O\textsubscript{4}:Eu\textsuperscript{2+}, producing a green phosphor with a visible brightness that lasted through the entire night. This increase in phosphorescence can be seen in figure 3.3 taken from the paper written by Matsuzawa.

Matsuzawa et. al needed to determine if the charge conducting species was the same for the Dysprosium co-doped phosphor as for the one that is only doped with europium. Instead of reproducing the Hall experiment that Abbruscato carried out, Matsuzawa instead performed a photoconductivity experiment. In order to use this experiment to determine the charge carriers they modified the standard photoconductivity experiment. The illumination was allowed to fall only on the half of the sample near the positive electrode, and then on the half of the sample near the neg-
Figure 3.3: The relative intensities of A: SrAl$_2$O$_4$:Eu$^{2+}$; B: SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$; C: SrAl$_2$O$_4$:Eu$^{2+}$, Nd$^{3+}$; D: the commercially available ZnS:Cu, Co; taken from the paper written by Matsuzawa. [4]
ative electrode. They then compared the two different photoconductivity results. It was determined that the conductivity was higher when the sample was illuminated on the half near the negative electrode. In this fashion they determined that the carriers must be the holes moving through the valence band. By measuring the photocurrent under varying temperature from liquid nitrogen, up to room temperature, they were able to determine that the activation energy for the holes was .03 eV.

As well as codoping the SrAl$_2$O$_4$:Eu$^{2+}$ with Dy$^{3+}$ samples were also made where the codoping agent was Nd$^{3+}$. In both cases it was determined by Matsuzawa that they both act as hole traps. In analyzing their thermal glow curves it was determined that the peak intensity occurred at 75$^\circ$ C for the dysprosium codoped sample and at 60$^\circ$ C for the neodymium codoped sample. The trapping level for the dysprosium doped sample turned out to be slightly deeper than that of the neodymium doped sample. This resulted in a longer phosphorescent lifetime for SrAl$_2$O$_4$:Eu$^{2+}$,Dy$^{3+}$. They determined the hole trap depth for this sample to be .65 eV.

Matsuzawa et al. estimated the band gap energy for the SrAl$_2$O$_4$ host at 6.5 eV. This was accomplished by analyzing the low energy edge of the Eu$^{2+}$ excitation due to the absorption of the host lattice. The phosphorescent mechanism for SrAl$_2$O$_4$:Eu$^{2+}$:Dy$^{3+}$ is interpreted in the following way. After exposure to UV excitation at 365nm the $4f \rightarrow 5d$ transition in the europium dopant occurred. This energy was not sufficient to excite the crystal host. Since it was assumed that the charge transfer mechanism is holes, the Eu$^{2+}$ is ionized and transformed into Eu$^{1+}$. The hole produced then moved into the valence band. The thermal activation energy for the hole is known to be 0.03 eV, so that $\Delta E$ from the ground state to the valence band is 0.06 eV. This is derived from the number of produced holes being equal to:

$$\exp \left( -\frac{\Delta E}{2kT} \right)$$ (3.1)

The hole will then move through the valence band until it is then trapped by a dysprosium ion. The trapping of this hole will convert our Dy$^{3+}$ into Dy$^{4+}$. When
the UV excitation is stopped the hole will be thermally re-excited from the trapping Dy$^{4+}$ ion and is then dropped back the 0.65 eV into the valence band. The hole will then travel back to the Eu$^{1+}$ ion where it is recombined. This produces the observed phosphorescence. This is shown schematically in figure 3.4

In this model the existence of the Dy$^{4+}$ as well as that of Eu$^{1+}$ are assumed to be stable in the host crystal. In 1968 L. P. Varga studied the existence of Dy$^{4+}$ in cesium Dysprosium heptafluoride [6] [7]. By analyzing the absorption spectra of this material Varga found numerous lines that were difficult to explain. Using recently created analyzation software, he was able to determine that these lines belonged to the tetravalent state of the dysprosium ion. This lead him to conclude that Dy$^{4+}$ can be stable in a host crystal. Matsuzawa used these papers to justify the creation of the Dy$^{4+}$ hole trapping ion.

Despite this early work on SrAl$_2$O$_4$:Eu$^{2+}$,Dy$^{3+}$ the mechanism behind the long phosphorescence had not been fully explored. Aitasalo et al. attempted to further the explanation of this mechanism in a paper they published in 2003 [8]. Some of the work that had been done ended up being contradictory or incomplete. The bulk of the work however, concluded that the charge transfer mechanism was a hole created from the Eu$^{2+}$ moving, either through the valence band, or directly to the trapping location. In order for this to occur it requires the creation of Eu$^{1+}$ and RE$^{4+}$, neither of which seemed like a very probable occurrence.

In order to get around this problem Aitasalo et al. came up with a new mechanism for the long phosphorescence. In their mechanism the traps were filled from the direct absorption of the excitation energy. This produced a hole in the valence band. The trapped energy was freed in a room temperature thermal process, allowing for an electron-hole recombination. This energy was then fed into the Eu$^{2+}$ rare earth ion causing the 4f5d excitation seen in the emission spectra of the phosphor. A schematic of this process can be seen in figure 3.5.
Figure 3.4: The schematic of the energy levels in SrAl$_2$O$_4$:Eu$^{2+}$,Dy$^{3+}$ phosphor as generated by Matsuzawa [4]
Figure 3.5: The schematic of the charge transfer mechanism proposed by Aitasalo et al. [8]
In 2005 a new argument was introduced into the debate about the charge transfer mechanism in SrAl$_2$O$_4$:Eu$^{2+}$. Dorenbos used newly developed techniques to determine the exact location of the lanthanide impurity levels in the band gap of the host crystal. With this new information Dorenbos concluded that the popularly accepted method of charge transfer must be wrong. In fact he concluded that; "Instead of hole transfer transport via the valence band it is shown that the mechanism must involve electron transport."[9] To reach this conclusion Dorenbos analyzed the energy level locations of the lanthanides inside the host band gap.

Dorenbos determines the energy levels using the following process. First the energy required to promote an electron from the valence band to a trivalent lanthanide is calculated. This created a divalent lanthanide. The next step was to calculate the energy required to promote an electron from the $4f^n \rightarrow 4f^{n-1}5^1$ energy levels. Finally, the energy required to ionize the divalent lanthanide was calculated. With the variation of the $f \rightarrow d$ energy, as well as the energy needed to promote an electron from the valence band to the trivalent lanthanide, and finally the type of ion and host lattice can used to derive a model that allow predictions of the energy level locations within the host band gap. Figure 3.6 shows the location of both the divalent, and trivalent lanthanides energy levels within the SrAl$_2$O$_4$ host crystal lattice.

Dorenbos proposed a new mechanism for the long persistent phosphorescence in SrAl$_2$O$_4$:Eu$^{2+}$,Dy$^{3+}$. In his proposal an electron located in the $4f^7$ energy level of Eu$^{2+}$ becomes excited by ambient light and is promoted to the $5d^1$ energy level. This electron will then be thermally promoted from the excited $5d^1$ level in to the conduction band. The electron will then migrate through the conduction band until it becomes trapped by a Dy$^{3+}$ ion. The electron remains in the newly created Dy$^{2+}$ ion until it is again thermally promoted into the conduction band. The electron then travels back through the conduction band until it recombines with a Eu$^{3+}$ ion. Once
Figure 3.6: The calculated divalent and trivalent energy levels of the lanthanide ions within the band gap of SrAl$_2$O$_4$, as calculated by Dorenbos [10]
recombined with the europium ion the electron will relax back to the $4f^7$ level from the $5d^1$ level, releasing a photon in the process.

A group lead F. Clabau analyzed SrAl$_2$O$_4$:Eu$^{2+}$,Eu$^{2+}$,Dy$^{3+}$ around the same time as Dorenbos was conducting his work. This group also noticed an effect reported by an early group lead by Poort. When the emission spectra of SrAl$_2$O$_4$:Eu$^{2+}$ is taken at temperatures below 250K a new peak begins to appear[11]. This peak is centered at 450nm and they determined that this peak can not be attributed to the normal Eu$^{2+}$ $4f^7 \rightarrow 4f^6 5d^1$ emission. This new peak can be seen in figure 3.7.

Clabau et al. proposed that excitation in the ultra-violet regime promoted electrons from the $4f^7$ energy level of the doped Eu$^{2+}$ to its $5d^1$ energy level. This caused an electron to be promoted from the valence band into an Eu$^{3+}$ defect ion. The electron promoted into the $5d^1$ energy level was then trapped in an oxygen defect site near the Eu$^{3+}$ ion. The hole that was created in the valence band was then trapped in either a strontium or aluminum defect site. The trapped electron was then thermally released directly to the $4f^6 5d^1$ level of the Eu$^{3+}$ which then relaxes back to the $4f^7$ energy level producing the commonly seen green emission as well as the 450nm emission reported by Poort er al.[11] This mechanism can be seen in figure 3.8.

This new mechanism was proposed to correct some inconsistencies in the original mechanisms after new experiments were conducted. In particular it was necessary to try to reconcile the idea of holes as the charge carrier with the new information about the location of the lanthanide energy levels in the forbidden band. In order to adapt to this, the trapping of electrons promoted to the $5d$ levels by UV excitation must be considered. However, there is still the issue of the photoconductivity experiments which showed that the holes were actually the charge carriers.
Figure 3.7: Plot of the secondary emission peak as seen by Clabau et al. The spectra has been fit with Gaussian’s showing the emission peaks.
Figure 3.8: Clabau et al’s mechanism for the long persistent phosphorescence. [12]
The work done on SrAl$_2$O$_4$:Eu$^{2+}$ showed a lot of promise as a new long persistent phosphor. However, when soaked for long periods in water the luminescence of this phosphor, and others like it, is greatly reduced. This makes the phosphor much less useful as a pigment for paint, and other industrial uses. In order to find a phosphor with better stability in water, groups began to experiment with a new phosphor, Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$. At room temperature these phosphors show very similar emission peaks to those of SrAl$_2$O$_4$:Eu$^{2+}$. Unfortunately under the initial manufacturing process the long persistent phosphorescence that made SrAl$_2$O$_4$:Eu$^{2+}$ so useful was not in evidence.

In 2001 a group lead by Yuahua Lin began experimenting with the formulation of Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$ by adding a codopant. They quickly found that when dysprosium was added to the formulation the lifetime of the emission spectra was increased dramatically. In fact they showed that when the ratio of Eu$^{2+}$ to Dy$^{3+}$ was 1 to 3 that not only was the length of the emission decay dramatically increased, but also the overall intensity of the emission was increased. This is evident in figure 4.1. In fact the emission from the phosphor is observable for up to 10 hours in a darkened room.

In order to explain this long phosphorescence the authors use the method proposed by Aitasalo et al. When the phosphor is illuminated a hole is formed from the Eu$^{2+}$ excitation. It is then trapped by either an oxygen vacancy, or by an alkaline earth cation vacancy. When these holes are released and recombine with an electron the energy of this recombining is transferred to an Eu$^{2+}$ ion promoting an electron from
Figure 4.1: The emission decay curves as found by Yuahua Lin et al. for varying ratios of Eu to Dy in Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$,Dy$^{3+}$ [13].
the $4f^7$ level to the $5d^1$ level. The observed emission occurs when this electron relaxes back to the $4f^7$ energy level.

In order to determine the trap depth of Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$ Hiroshi Furusho et al. analyzed the trap depth of the defect sites in the host lattice. To do this they performed temperature dependant studies analyzing the persistent phosphorescence of the material. When the phosphor was cooled to below 150 K almost no persistent luminescence was observed. As the temperature is increased the persistent phosphorescence begins to be seen at around 200 K to 210 K. As the temperature continues to increase so does the phosphorescence intensity, as well as the duration until a temperature of 250K is reached. At this point the intensity plateaus through room temperature, or about 300 K.
Chapter 5

New Work

5.1 Formulation

The samples used in this work were prepared by General Electric, under the direction of Anant Sethur. The $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ samples were produced using standard ceramic synthesis. Highly pure samples of $\text{SrCO}_3$, $\text{Eu}_2\text{O}_3$, $\text{Sm}_2\text{O}_3$, $\text{Y}_2\text{O}_3$, $\text{Gd}_2\text{O}_3$, $\text{MgO}$, and silicic acid were mixed together and fired at $1200 - 1300\, ^\circ\text{C}$ in a reducing gas of $\text{N}_2/\text{H}_2$. The samples were then ground into a powder and refired at the same temperature. Enough europium was included to replace the strontium at one molar percent. This is also the case for any other rare earth codopant. So we had two different formulations to analyze $(\text{Sr}_{0.99}\text{Eu}_{0.01})_2\text{MgSi}_2\text{O}_7$ and $(\text{Sr}_{0.98}\text{Eu}_{0.01}\text{Sm}_{0.01})_2\text{MgSi}_2\text{O}_7$. The samples for the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ formulation were also produced using the standard ceramic synthesis.

5.2 Experiments

After the samples were synthesized, cursory excitation and emission curves, as well as the diffuse reflectance measurements were performed at GE. The luminescence measurements were taken using a SPEX Fluorolog2 spectrometer, using a xenon bulb as the excitation source. The measured emission was then corrected for the lamp output and recorded. The diffuse reflectance of the sample was taken using a Perkin-Lambda 800. The reflectance was standardized using $\text{BaSO}_4$ powder. The room temperature lifetime measurement was taken by exciting the sample with a pulsed PicoQuant laser with an emission at 394 nm, and then measuring the emission.
with a thermoelectrically cooled R928-P Hamamatsu photomultiplier tube (PMT) attached to a Edinburgh F900 spectrometer. These initial measurements showed the samples to have a single, broad emission peak located around 500 nm, with the main excitation peak occurring at approximately 410 nm.

To confirm the initial measurements made at GE the excitation spectra of the \( \text{Sr}_{2}\text{MgSi}_2\text{O}_7: \text{Eu}^{3+} \) was measured using a Cary 14 spectrophotometer. A tungsten lamp was used as the visible wavelength excitation source, while a deuterium lamp was used to measure the ultraviolet (UV) excitation. A thermoelectrically cooled Hamamatsu R636-10 PMT was used to measure the sample emission. Once again the sample was held in the Oxford CF1404 continuous flow cryostat. A Corion 900LP dichroic filter was used in front of the PMT. The lamp output was calibrated using a silicon diode, with a known spectral response. Similar techniques were used to verify the \( \text{SrAl}_2\text{O}_4: \text{Eu}^{2+} \) samples also sent.

Once the initial measurements were made, and the samples were confirmed to have the proper optical characteristics, they were shipped to UGA. Based on the emission and excitation curves from GE, the variable temperature lifetime analysis of \( \text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{3+} \) was preformed. The sample was placed in an Oxford model CF1204 continuous flow cryostat. A 398 nm light emitting diode (LED) was used as an excitation source. The light was sent through a narrow band interference filter to limit the excitation wave length. The filter was centered at 410 nm with a full width half max (FWHM) transmission window of 10 nm. The emission from the sample was also filtered through a narrow band interference filter, this time centered at 500 nm ±10 nm. Finally the emission signal was detected using a Hamamatsu R212 PMT.

The LED was pulsed at approximately 100 KHz using an Avtech nanosecond pulse generator. The pulsed signal from the generator was then amplified through an Avtech amplifier generating a pulse of approximately 5 V. The amplified pulse is then used to power the LED. The signal from the PMT is fed into an EG&G quad fast
timing amplifier model FTA 410. From the amplifier the signal is sent into an EG&G model T121/N quad updating discriminator to filter the dark background current generated by the PMT. After the discriminator the signal is fed into an EG&G Ortec 567 TCA/SCA time to amplitude convertor. The incoming PMT pulse is used as the start signal for the TAC while the stop signal is produced by the synchronization pulse of the Avtech amplifier. In this way it is assured that every pulse generated by the PMT was measured. Finally the signal is fed into an Ortec multichannel scaler card, the pulse height from the TAC was converted into a pixel location, and the lifetime was measured and displayed. The temporal response of the entire lifetime setup was measured to be < 2 ns. Figure 5.1 shows a schematic drawing of the experimental setup.

After measuring the lifetime of the Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$, I placed the Sr$_2$AlO$_4$:Eu$^{2+}$ sample into the same lifetime set up. There are two excitation peaks for the SrAl$_2$O$_4$:Eu$^{2+}$ sample so I had to change the excitation filters in the set up. To check the lifetime of the first site I used a 400nm LED with a 400nm narrow band filter with a full width half max of 10nm. To determine the lifetime of the second excitation peak I used a 423nm LED with a narrow band filter of 430nm. Also since the luminescence of this material does not fully quench until a temperature of around 400K I needed to use a small clam shell furnace to heat the sample to these temperatures. Figure 5.2 shows the two different sets of lifetime data. Because of the existence of the second emission peak in SrAl$_2$O$_4$:Eu$^{2+}$ it was determined that Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$ should be the focus of the work, since the analysis of only one emission peak would be more straight forward.

I next used a modified version of thermally stimulated luminescence, (TSL), called infra-red stimulated luminescence, (IrSL), to determine the photo-ionization threshold for SrAl$_2$O$_4$:Eu$^{2+}$. This experimental setup was created at UGA in Uwe Happek’s lab. The exact nature of the experiment will be discussed in future work. In the IrSL
Figure 5.1: A schematic drawing of the lifetime experimental setup.
Figure 5.2: This figure shows the lifetime for Site I, the square black points, and Site II, the orange circles.
experiment the sample was placed in the same Oxford model CF1204 cryostat used in the lifetime experiment. A 300 watt xenon lamp was used to illuminate the sample. The light from the xenon lamp is first sent through a 305 long pass filer and then is sent through 2 Mcpherson model 272 monochrometers. The incoming slit on the first monochrometer was set to 1mm, while the slit in between the two monochrometers was set to 2mm. Finally the out coming light slit was set at 1mm giving a total dispersion for the output wavelength of approximately 1.5nm. A Hamamatsu R212 PMT charged to 900V was position perpendicular to the incoming light. A 500nm narrow band filter was placed between the sample and the PMT. A 785nm laser diode was set so that the beam would enter the cryostat through the window 180° from the window letting in the excitation light. The laser’s beam is fed through a small iris followed by an RG815 Schott glass filter. The Schott glass filter prevents any stray room light from entering the cryostat when the laser is on. A schematic of the experiment is shown in figure 5.4

The sample is cooled to 80K using liquid nitrogen. While this occurs the sample is turned to face the laser beam, and the laser is turned on for 10 minutes, emptying any filled traps in the sample. When the sample is cold, the laser is turned off, and the sample is turned to face the xenon lamp. The lamp is turned on and the sample is illuminated for 300 seconds. After 5 minutes the shutter on the monochrometer is closed, the filter wheel is turned until the light is blocked, and the sample is rotated 135° so that is between the PMT and the laser. The shutter for the PMT is opened, the multichannel scaler card is started, and then the laser is turned on. The laser will then empty any traps near the conduction band, If any were filled. If only the dark current from the PMT is measured, then the sample is rotated back to face the light source, the incoming wavelength is lowered, and another trial is run. If, however a signal is seen than we know what wavelength is sufficient to excite electrons from their ground state to the conduction band. This will then determine the energy difference
from the ground state to the conduction band. The plot on figure 5.3 shows the onset of photo-ionization for site II in SrAl$_2$O$_4$:Eu$^{2+}$.

The next set of experiments were conducted by Long Pham, and were performed in the infrared regime. The samples were placed in the same Oxford model CF1204 continuous flow cryostat used in the visible lifetime measurements. To take the infrared emission measurements a SPEX 500M monochromator was used with a 300 groove per centimeter diffraction grating installed and an entrance slit width of 10 nm. The emission spectra was collected using a liquid nitrogen cooled charge coupled device (CCD) attached to the monochromator. The sample was excited using a Hitachi HL6314MG laser diode at 635 nm with a 3mW peak intensity. An RG695 Schott glass filter was used to filter out the laser peak, and to allow the infrared emission to be transmitted. A second emission scan was taken later, using a helium nitrogen (HeNe) laser instead of the Hitachi laser diode. With the HeNe laser, a Semrock 633nm Raman filter was used to block the laser peak from entering the monochromator. The slit width was also increased to 200 nm.

Finally, the lifetime of the sample was measured, in the infrared, using the same Oxford cryostat as before. The emission from the sample was sent through the same SPEX 500M as in the emission experiment. The excitation pulse was generated with the Hitachi laser diode. The thermoelectrically cooled R636-10 PMT was used as the detection device. The output signal from the PMT was fed into an amplifier, from there into a fast amplifying discriminator, and from there was used as the start pulse for another Ortec TAC/SCA 567 time to amplitude convertor. An HP function generator was used to pulse the laser diode, and again, the synch signal from the pulse generator was used as the stop pulse for the TAC. The synchronization signal was inverted to match the polarity.
Figure 5.3: The onset plot for SrAl$_2$O$_4$:Eu$^{2+}$. We can see that photo-ionization begins to occur around 470 nm
Figure 5.4: A schematic drawing of the IrSL setup
Chapter 6

Results

The excitation and emission curves, seen in figure 6.1, taken at GE were in agreement with those taken in previous literature about this sample. This was taken to confirm the composition of the sample. This tells us that our sample was produced properly. In an analysis of the emission and excitation spectrum we notice a large spectral overlap between the two. This makes it very difficult to determine an exact value for the Stokes shift, but does tell us that if there is a shift in the Eu$^{2+}$ emission levels it is very small. A small Stokes shift means that a nonradiative decay through level crossing is very unlikely. Despite this, thermal quenching of the emission has been reported at temperatures as low as room temperature.

When we cool the sample to liquid nitrogen temperatures ($\sim$ 80K) we find the phosphorescent lifetime to be approximately 600 ns. As the temperature rises, in particular as we approach a temperature of 200 K, we see that the decay profile changes from a single exponential function to a stretched exponential with a quick initial component and a much longer baseline that comes from the intrinsic Eu$^{2+}$ luminescence. This is evident if we look at the plots in figure 6.2. We can analyze these decay times a little easier if we fit the first part of the curve to a fixed exponential decay curve which will produce an initial decay time, and reduce the contribution of the Eu$^{2+}$ lifetime. This analysis fitting the lower temperature decay curves well, however at higher temperatures the fast component is overestimated. This phosphorescence is a clear indicator of the trapping/detrapping process of the excited $4f^7 \rightarrow 4f^65d^1$ electrons.
Figure 6.1: The excitation and emission spectra for $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$. 
Despite the stretched exponentials so common in long luminescent phosphors it is still very difficult to interpret the mechanics behind them. In an attempt to determine the origin of the afterglow we see that as the lifetime begins to go down, there is a corresponding increase in the phosphorescent intensity. This can be seen clearly in figure 6.2. At low temperatures the excitation energy may not be high enough to promote the mobile charge carriers directly to the trapping level. Further, any mobile charge carrier that does get promoted to the trapping level is unable to escape this level without thermal activation. This is why at temperatures below 200K we see a single exponential decay profile. This decay profile matches that expected for the \( \text{Eu}^{2+} \ 4f^7 \rightarrow 4f^5d^1 \) excitation. As the temperature increases there is more thermal energy available to overcome the trap depth and so we see a reduced initial decay time, with a corresponding increase in the overall phosphorescent intensity.

After fixing the fast component of the decay we can analyze the slower component to get an estimate on the non-radiative decay rate. To do this we will first plot the lifetime as a function of temperature. We will then fit this plot with an Arrhenius curve given by

\[
y = \frac{1}{x_0 + y_0 \exp\left(-\frac{E_a}{kT}\right)}
\]  

(6.1)

In this equation the \( x_0 \) term is the inverse of the low temperature radiative rate, in this case \( x_0 = 600\text{ns}^{-1} \) or a decay time of 600ns at low temperatures. The \( y_0 \) term is the escape frequency, here \( 3.9814 \times 10^{10} \) Hz. Finally we have the \( E_a \) term which is the activation energy. For \( \text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{3+} \) this turns out to be, when converted in to electronvolts, 0.2 eV. The plot of the lifetimes as well as the corresponding Arrhenius fit is shown in figure 6.4. The activation energy found here is in good agreement with the theoretical energy barrier for \( \text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{3+} \). Also the attempt frequency found here is in reasonable agreement for most divalent lanthanides. These values lend strong credence to the proposed mechanism of \( \text{Eu}^{2+} \) photoionization into the
Figure 6.2: A plot of the luminescent decay curves at 300K and 110K
conduction band, which is the proposed first step in the long phosphorescence in 
$\text{Sr}_2\text{MgSi}_2\text{O}_7\text{:Eu}^{3+}$.

The lifetime experiments run on $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{:Eu}^{3+}$ do not offer any direct evidence of electrons being promoted into the conduction band. Also the work discussed here does not address the role of trivalent rare earth ions. We can determine their effect on $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{:Eu}^{3+}$ when we analyze $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{Eu}^{3+}\text{Sm}^{3+}$.

When we examine the $\text{Eu}^{2+}$ excitation curve after adding $\text{Sm}^{3+}$ to $\text{Sr}_2\text{MgSi}_2\text{O}_7\text{:Eu}^{3+}$ we find almost no change in the emission spectra. However we do notice a reduction in the overall intensity of the emission by a factor of around 5 compared to those samples without Samarium. One possibility for the reduction in intensity is that the addition of $\text{Sm}^{3+}$ creates lattice defects in the host crystal which are deep electron traps. However, when we add $\text{Y}^{3+}$ and $\text{Gd}^{3+}$ we see no strong decrease in the luminescent intensity, and in fact if we add $\text{Dy}^{3+}$ or $\text{Nd}^{3+}$ we see an increase in the phosphorescent intensity.[13] With this we can conclude that the $\text{Sm}^{3+}$ ions are in fact the charge trapping center, and do not produce secondary lattice defects that act as traps. We know that $\text{Sm}^{3+}$ is a deep electron trap, which helps lend credence to our conclusion that charge carriers promoted after $\text{Eu}^{2+}$ $4f^{7} \rightarrow 4f^{6}5d^{1}$ excitation are the electrons promoted into the silicon conduction band.[14]

This conclusion can be directly verified when we look at the absorption spectra in the visible as well as near infrared spectra, after first exciting the $\text{Eu}^{2+}$ $4f5d$ band with 410 nm wavelength light. This absorption onset occurs at 12500 cm$^{-1}$ or about 800 nm. If we instead start with a dark sample, and illuminate it at 520 nm, outside of the $\text{Eu}^{2+}$ excitation range, we do not see any new absorption bands. This is clearly seen on the absorption plot in figure 6.5. We can conclude that this absorption band is due to $\text{Sm}^{2+}$. In a paper written in 2003 Dorenbos determined that[15]

$$5d(\text{Eu}^{2+}) = 5d(\text{Sm}^{2+}) + 9840 \text{ cm}^{-1}. \quad (6.2)$$
Figure 6.3: Plot of the lifetimes as well as the normalized intensity as a function of temperature.
Figure 6.4: Plot of lifetime versus temperature with the Arrhenius fit. From equation 6.1 we have $x_0 = 600 \text{ ns}^{-1}$, $y_0 = 3.9814 \times 10^{10} \text{ Hz}$, and $E_a = .2 \text{ eV}$
Since we know that the Eu$^{2+}$ transition in Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$ is 22500 cm$^{-1}$ we can calculate that the onset of Sm$^{2+}$ $4f^6 \rightarrow 4f^55d^1$ transition in Sr$_2$MgSi$_2$O$_7$:Eu$^{3+}$ is at 12500 cm$^{-1}$. If this is assigned to the SmA band, which is the weaker of the two samarium sites, then we have the SmB site at 13850 cm$^{-1}$ or 720 nm. If we look at the absorption spectra in figure 6.5 we see that this corresponds very well to the onset of the absorption peak of Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$:Sm$^{3+}$. While it is possible that this absorption peak arises from a direct energy transfer from the Eu$^{2+}$ ion to the Sm$^{3+}$ this does not seem likely. This effect occurs at low temperatures, and the inter-ion distance between the two ions is about 25 Å, therefore, it is most likely due to the trapping of mobile electrons after Eu$^{2+}$ photoionization.

It has been shown that Sm$^{2+}$ is stable for at least 2 days, when the phosphors are isolated in a dark room, and held at room temperature. This corresponds to very deep electron traps. By looking at the optically stimulated luminescence of the Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$:Sm$^{3+}$ and comparing it to the diffuse reflectance of the same sample, we see a very nice correlation between the two. From this comparison we see that the centers for the photostimulated luminescence (PSL) in this phosphor is the Sm$^{2+}$ which are created after the photoionization of the Eu$^{2+}$ into Eu$^{3+}$. This is yet another proof that the charge carrier traps are Sm$^{2+}$ and not lattice defect sites. The final point to be made is that even though Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$ samples with no RE$^{3+}$, or even those with Y$^{3+}$ or Gd$^{3+}$, still show a measurable photostimulated luminescence, they are at least an order of magnitude lower in intensity.

With this PSL data in hand we have the experimental proof of the mechanism behind the persistent phosphorescence in which photoionized electrons from Eu$^{2+}$ are trapped by an RE$^{3+}$ ion. The only difference between the different RE$^{3+}$ ions is in their relative trap depth. For ions like Dy$^{3+}$ or Nd$^{3+}$ with trap depths that are close to the conduction band using them to codope Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$ they can be depopulated thermally as opposed to optically. This allows for numerous trapping
Figure 6.5: The absorption and diffuse reflectance scans performed on a dark sample, after a 520nm or a 410nm excitation.
Figure 6.6: A plot of the optically and photostimulated luminescence of Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$ and Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$:Sm$^{3+}$
and detrapping events. Because of this we get persistent phosphorescence of $> 20$ hrs in these phosphors.
Chapter 7

Conclusion

Results for the experiments performed at GE and UGA have demonstrated that the mechanism behind the long phosphorescence of Sr$_2$MgSi$_2$O$_7$:Eu$^{3+}$ is due to the photoionization of Eu$^{2+}$ into the conduction band. Electrons in the conduction are free to move until they either recombine with an ionized Eu$^{2+}$ or are trapped by RE$^{3+}$ ions, such as Sm$^{3+}$, Dy$^{3+}$, and Nd$^{3+}$, that were added as a codopant. Once trapped the electrons are held until enough thermal energy is provided to release the electron back to the conduction band. Once again the electron is free to move, until it recombines with the photoionized Eu$^{3+}$ ions. Because the experimental results for the 4$f^n$ ground states of the RE$^{2+}$ ions agree well with their estimated locations in the band gap, we have the potential to extend this to other compositions of long persistent phosphor’s using Eu$^{2+}$. In particular since similar PSL measurements have been observed in SrAl$_2$O$_4$:Eu$^{2+}$:Sm$^{3+}$ we can conclude that electrons must be the charge transfer mechanism in this phosphor as well. We also see that there is the possibility of replacing the current standard of sulfide phosphors as a practical infrared storage material, with a phosphor having greater environmental stability.
Bibliography


