INVESTIGATION OF Ca₂Si₃P₂O₉:Eu²⁺ FOR APPLICATION TO THE PLASMA DISPLAY PANEL

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INVESTIGATION OF Ca_{2-x}Sr_xP_2O_7:Eu^{2+} FOR APPLICATION TO THE PLASMA DISPLAY PANEL.

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To my Father, Richard Allen Gilstrap
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SUMMARY

The techniques of Vacuum Ultraviolet (VUV) photoluminescence excitation (PLE) and emission (PL) spectroscopy, x-ray diffraction, and scanning electron microscopy (SEM) were used to evaluate the effectiveness of $\text{Ca}_2\text{Sr}_x\text{P}_2\text{O}_7:\text{Eu}^{2+}$ as a blue component PDP phosphor. The above notation denotes (host lattice : activator).

Phosphor samples with a high degree of crystallinity were synthesized via a solid-state reaction technique in which luminescent α-phase formation was found to depend on the firing procedure and ratio of anion to cation (AC) utilized. The boundary of allowed AC ratio ($1.03 < AC < 1.09$) was found to vary with firing time due to volatilization of the oxides of phosphorus at temperatures above 1000°C. Examination indicated that compound phase had a significant impact on the surface morphology of phosphor powders produced in $\text{Ca}_2\text{Sr}_x\text{P}_2\text{O}_7:\text{Eu}^{2+}$. The strongly luminescent α-phase was characterized by a smooth surface morphology while the weakly emitting β-phase structure displayed a rough character typified by sharp edges.

Photoluminescence excitation (PLE) analysis of the $\text{Ca}_2\text{P}_2\text{O}_7:\text{Eu}^{2+}$ end-member composition revealed well defined host and activator absorption features. Host-sensitization bands corresponding to $\text{P}_2\text{O}_7^-$ and $\text{CaO}$ complexes were observed at 125nm and 175nm, respectively. This indicated that efficient transfer of VUV energy from the host lattice to substituted $\text{Eu}^{2+}$ activator ions was occurring through a non-resonant multipole exchange mechanism. Additionally, a broad absorption band starting at 200nm and progressing to longer wavelengths was observed and attributed to direct excitation of the $5\text{S}_{7/2}(4f^7)$ ground state configuration of $\text{Eu}^{2+}$ to the $4f^5\text{d}$ excited state. A prominent dip in the spectra at 290nm confirmed the crystal field splitting of $t_{2g}$ and $e_g$
orbitals into higher and lower energies, respectively. Photoluminescence emission analysis of α-phase samples in Ca₂Sr₃P₂O₈:Eu²⁺ produced a photon emission profile that departed significantly from the linear variation predicted by theoretical crystal field strength calculations. This range followed a parabolic emission trend that began at 415nm (Ca₃P₂O₈:Eu²⁺) and progressed through a maximum of 441nm (CaSrP₂O₈:Eu²⁺) before returning to 420nm (Sr₃P₂O₈:Eu³⁺). Through the application of semiconductor band-gap theory, it was determined that this behavior could be attributed to an aperiodic perturbation of the crystal potential arising from disorder in the system. Additionally, the influence of Type I stress fields at Eu³⁺ sites was identified through PLE analysis.

The 441nm emission of CaSrP₂O₈:Eu²⁺ was increased by 80% through the application of optimization procedures involving Eu²⁺ concentration, AC ratio, and flux addition. The relative quantum efficiency of host-sensitization bands corresponding to (P₂O₇)⁴⁻ and CaO complexes was increased by 214% and 173%, respectively. Calculation of the CIE coordinates corresponding to the 441nm emission from CaSrP₂O₈:Eu²⁺ produced values of x = 0.16 and y = 0.046. These results indicated that the chromaticity of this europium doped pyrophosphate compares favorably to the current blue component PDP phosphor, BaMgAl₁₂O₁₉:Eu²⁺ (BAM). Comparison of PLE spectra indicated that the luminescence efficiency of phosphate host-sensitization and direct Eu²⁺ excitation bands in CaSrP₂O₈:Eu²⁺ was higher than the host and activator absorption features observed in BAM. However, the bottom of a sharp optical absorption edge associated with the phosphate band was found to correspond with the 147nm primary PDP excitation line and resulted in a dramatic loss of emission intensity. Evaluation of the thermal stability of CaSrP₂O₈:Eu²⁺ indicated that a 6% loss of emission intensity
occurred following a simulated burn-in procedure, whereas, BAM lost 37% of its original luminescent output.
CHAPTER 1
INTRODUCTION

After decades of research and development, plasma displays are rapidly appearing in the commercial and consumer markets. Plasma display panels (PDPs) have finally achieved luminance and efficiency values on par with high definition cathode ray tube (CRT) monitors. The PDP provides for an extremely large viewing area and angle while maintaining a very shallow unit depth. An advantage of the PDP over other types of flat panel displays (FPDs) is that the capacitance between the electrodes is relatively small which makes driving a large display area less difficult and therefore leads to lower energy consumption.

As the name suggests, the PDP utilizes a high-energy plasma discharge, which generates UV photons that excite phosphors for the primary colors of Red, Green, and Blue. This RGB set is utilized in virtually all full color display devices. These high energy photons (147nm) impose unique requirements on PDP phosphors as will be discussed in some detail in subsequent chapters. A necessary step in panel manufacture involves the heating of phosphors to 500 °C for the purposes of panel sealing, increasing phosphor to substrate adhesion, and complete elimination of organic additives. Although, the red and green component phosphors show little degradation in their properties following this heating process, the blue PDP phosphor BaMgAl₁₁O₁₉:Eu²⁺ (BAM) suffers losses in luminescence efficiency of 30% or more. This deterioration of the blue luminescence component is one of the most significant shortcomings in current PDP technology.
Initial investigations into the mechanisms of this effect by Oshio indicated that the oxidation of Eu from the 2+ valence state to 3+ was responsible. It was proposed that this would induce both non-radiative energy transfer and shared excitation between Eu$^{2+}$ and Eu$^{3+}$ luminescent centers. However, recent work by other investigators has produced strong evidence that the degradation in BAM performance is a function of the breakdown in local compound structure at Eu$^{3+}$ sites. This indicates that a new blue component PDP phosphor is required to replace BAM. Consequently, many research efforts are being directed to the discovery of novel blue emitting phosphors capable of efficient performance within the high energy PDP environment. Most importantly, the successful PDP phosphor must maintain this efficiency throughout the panel manufacturing process.

The phosphate class of phosphors was extensively studied for application to the fluorescent lighting industry due to favorable performance during both tube manufacturing and operational environments. Rare earth activated lanthanum phosphate, for example, is commonly used in compact fluorescent lamps, in which the wall temperature reaches up to 200 °C during operation. At these temperatures, most phosphors degrade but the terbium activated lanthanum phosphate exhibits highly stable luminescence characteristics. Additionally, several phosphate phosphors were found to retain approximately 90% of their luminescent efficiency following a burn-in step that is very similar to that utilized in PDP manufacture. A recent theoretical work on LaPO$_4$ and AlPO$_4$ indicated that these materials have the lowest conduction band (E_g), which possesses predominantly phosphate-like character, located at 7 – 7.5 eV above the valence band edge. These theoretical results were also confirmed by VUV reflectivity
measurements, which show an intense absorption band near 150 nm. Accordingly, it was theorized that the 147 nm VUV excitation of the Xe plasma utilized in the PDP may produce efficient band-to-band excitation in many phosphate phosphors.

The emission characteristics of the pyrophosphates of Ca and Sr were studied in the early 1970's for potential application to the fluorescent lamp industry. A blue emission was found in several compositions doped with divalent Europium under 254nm excitation. The function of the host lattice in this spectral region was simply to hold the activator in place as Eu³⁺ directly absorbed UV energy. It was proposed that the application of higher energy excitation (147nm) would alter this absorption mechanism significantly. Additionally, an emission peak shift observed in a previous study on the Ca₅Sr₂P₂O₇:Eu composition range presented an opportunity for precise chromaticity tuning within the blue spectral region desired.

This thesis is focused on the europium-doped pyrophosphates as a potential replacement for the current blue component PDP phosphor, BAM. The key difference in the present study relative to previous investigations performed under 254nm excitation is the role played by the host lattice in energy absorption and transfer. The sensitive nature of the Eu³⁺ ion to the crystal field surrounding it requires the host lattice to be of single phase character and free of any impurities. Accordingly, the production of a pure phase sample space is a prerequisite for the accurate study of a pyrophosphate phosphor under 147nm excitation as any luminescent performance found must be due to intrinsic properties of the pure phase compound only. X-ray diffraction was the primary method of phase identification in this endeavor. Determination of the absorption properties of the host lattice group follows with photoluminescence excitation spectroscopy as the analysis
method utilized. Emission properties of the Eu$^{3+}$ activator within the pyrophosphate lattice were determined with photoluminescence spectroscopy.

Particle size and morphology information was provided through the use of Scanning Electron Microscopy (SEM) equipment, that utilizes low voltage capability. Thermal degradation effects were studied through a burn-in simulation in which pure phase samples are subjected to annealing at 500°C for one hour in an oxidizing environment as is encountered in the actual manufacturing of PDP screens. Comparisons to the current commercial phosphor (BAM) were then made. The phosphor systems examined in this work were synthesized by the solid-state reaction technique.

Background information regarding luminescence theory, characteristics of the alkaline earth pyrophosphates, the mechanisms of PDP operation, and specific requirements placed on PDP phosphors are presented in the next chapter. This will provide a suitable foundation for the interpretation of data presented in subsequent sections. Experimental procedure and equipment utilized is discussed in chapter 3 and encompasses both synthesis and analysis of phosphors. Chapter 4 is dedicated to the presentation of both experimental methodology and results obtained. Additional theory required for the interpretation of structure and spectral data is presented as well. Conclusions regarding both specific and overall results are presented in chapter 5. Future work to be addressed is provided in chapter 6.
CHAPTER 2
BACKGROUND

2.1 Introduction

It was in 1888 that the German physicist, E. Wiedemann, devised the term luminescence, which originates from the Latin word “lumen” or light. He described the phenomena of light emission, including both phosphorescence and fluorescence, as one that is not exclusively conditioned by a rise in temperature. In modern usage, luminescence with an afterglow that can be detected by the human eye is called phosphorescence and one that cannot is called fluorescence. Luminescence is defined generally as the emission of an excited material over and above the thermal background of radiation. Depending on the excitation mechanism, this process can be divided into various types: photoluminescence, electroluminescence, cathodoluminescence, thermoluminescence, triboluminescence, chemiluminescence, and bioluminescence. The prefixes indicate the manner of excitation that leads to light (photon) emission. A material that exhibits strong luminescence is known as a phosphor. Photoluminescence is produced by a phosphor which has been excited due to the absorption of light (photons). Electroluminescence describes the generation of light by application of an electric field to a phosphor and cathodoluminescence is produced when high energy electrons impinge upon a phosphor. Application of thermal and mechanical energy, leads to thermoluminescence and triboluminescence, respectively. And chemical or biological processes within a phosphor system generate chemiluminescence and bioluminescence, respectively. Photoluminescence is of primary importance for this work.
2.2 Photoluminescence

We can, as a general rule, divide inorganic solids into two classes: those which absorb light, and those which emit light. In both cases, controlled amounts of transition metal ions are added in order to control the photon absorption and/or emission properties of that solid\textsuperscript{11}. According to Huygen's principle of electromagnetic radiation scattering, photon irradiation of a solid causes the electric and magnetic field vectors of incident photons to couple with the wavevectors of electrons associated with the atoms comprising the solid. The incident radiation may interact with the solid through four components (refraction, scattering, transmission, and absorption). The exact amount of energy extracted from the incident radiation by each process is a complex set of variables dependent upon the type and arrangement of atoms comprising the solid. The reflectance of the photon is a function of the nature of the material surface, whereas absorption depends upon the interior composition of the solid. Accordingly, a resonance condition must exist before the impinging radiation can transfer energy to the solid leading to absorption of the photon. If the solid is an efficient phosphor, most of the incident radiation quanta will be absorbed and then subsequently emitted at a lower energy (longer wavelength) state as some energy is lost to phonon creation. In this respect, a photoluminescent phosphor may be viewed as a "photon-converter" in which the emitted electromagnetic radiation is primarily in the visible range, although other spectral regions such as the ultraviolet or infrared may be achieved as well\textsuperscript{12,13}.

The physical structure of the typical photo-phosphor particle can be generalized by a periodic lattice structure doped with small amounts of a luminescent ion. This ion is
known as the activator whereas the larger periodic structure is termed the host lattice. The activator center in an inorganic phosphor is a substitutional atom, located at a cation site in the lattice and is typically a transition metal or rare earth ion. A simplified two level energy scheme can be used to represent a photoluminescent phosphor system (figure 2.1a). The energy of the emitting system is raised from the ground state $g$ to the excited state $e$ by the absorption of photons. Radiation is emitted as the system relaxes back to the ground state. The time the system spends in the excited state is called the radiative lifetime, $\tau_{rad}$ of that state. Depending on the nature of the ground and excited states, the lifetime of the system may vary from $10^{-10}$ to $10^{-1}$ seconds. If this lifetime is in the range of $10^{-10}$ to $10^{-5}$ seconds, the radiation is termed fluorescence. For a lifetime ranging from $10^{-5}$ to $10^{-1}$s, the decay is described as phosphorescence. If, however, in addition to the excited state $e$, there exists another state $m$ slightly lower in energy, the lifetime of the system may be minutes or even days. Accordingly, $m$ is called a metastable state. In this system, the application of light or an electric field can raise the system to state $e$ which then decays to state $m$ through phonon emission. The transition from $m \rightarrow g$ is not allowed (by definition of metastable), so an energy $\Delta E$ must be supplied to raise the system back to state $e$ for emission to take place. After $\Delta E$ has been supplied by random thermal fluctuations, phosphorescent radiation results$^{14}$. This case is illustrated in (Figure 2.1b). For a lifetime ranging from $10^{-5}$ to $10^{-3}$s, the decay may be fluorescence or phosphorescence.
Figure 2.1: Simplified two-level energy system in a phosphor indicating absorption of energy and emission of a photon (a) and a similar system with a metastable energy level (b).
2.3 Optical Processes in Phosphors

2.3.1 Introduction

The general case of energy absorption and photon emission known simply as luminescence, occurs primarily by excited migration and electron-hole recombination processes. When the activator or luminescent centers in a phosphor material become close, the wave functions of their energy levels overlap considerably. These overlapping processes lower the energy of the optical absorption edge and promote delocalization of the charge carriers of excited luminescent centers\textsuperscript{15,16}. Consequently, the system is best described with an energy band model. When the electrons are promoted to the empty conduction band, they leave holes in the completely filled valence band. Because recombination occurs close to, or at defects in the crystal lattice, it has been the practice to distinguish near-edge emission, or emission with energy close to the energy gap \( E_g \), from deep center emission where the emitted energy is considerably less than \( E_g \)\textsuperscript{17,18}. Once excited, the activator may give up its energy radiatively through the emission of a photon or non-radiatively, in which only phonons are produced. The radiative efficiency is defined as

\[
\eta_{rad} = \frac{\text{Total number of photons emitted}}{\text{Total number of excited centers}} = \frac{1}{\tau_{rad}} \int \frac{L_{\text{ph}}}{I_0} \, dt ,
\]

(2.1)

where \( \tau_{rad} \) is the intrinsic radiative lifetime and \( \int L_{\text{ph}} / I_0 \) is the area under the normalized photoluminescence decay curve\textsuperscript{14}. Figure 2.2 illustrates the radiative mechanisms that may occur within an excited phosphor system.
Figure 2.2: Radiative recombination mechanisms in a phosphor: (a) band-band (b) band-acceptor (c) donor-band (d) donor-acceptor pair and (e) intra-ionic or localized transition.
2.3.2 Recombination Processes

2.3.2.1 Excitons

The exciton forms the basis for all optical transitions and thus, it is appropriate to treat this topic first. An exciton is an electron-hole pair bound together by a Coulomb force between the electron and hole. The exciton may be classified into one of two categories: free excitons or impurity-bound excitons. A free exciton, also called a Mott-Wannier exciton, is typified by the movement of both the electron and hole in extended orbits by migrating from atom to atom in a solid\textsuperscript{14}. In this respect, the free exciton may be regarded as an excited state of the entire solid. The energy levels for this system may be represented by those of the hydrogen atom. An exciton may become bound to an impurity forming an exciton-impurity complex if the presence of such an impurity increases the exciton binding energy. These bound or Frenkel excitons now have compact orbits, in contrast to the extended orbits of Mott-Wannier excitons. Numerous bound exciton complexes may be formed and the energies of these complexes are specific to the particular type of impurity involved\textsuperscript{19}.

2.3.2.2 Band-Band Transitions

Band-band transitions, (Figure 2.2a), are optical transitions which take place between the conduction and valence bands of the host material. Band-band absorption and emission processes are essentially the creation and annihilation of electrons in the conduction band and holes in the valence band, respectively. Band-band transitions may be classified into one of two classes: direct transitions or indirect transitions. Direct
transitions occur in both direct and indirect band gap materials whereas indirect transitions typically only take place in indirect band gap materials. In all transitions, the conservation of energy and momentum laws must be satisfied.

2.3.2.3 Band-Impurity Transitions

Band-impurity transitions are, in many respects, very similar to band-band transitions. However, the final state in a conduction band-acceptor transition is an impurity level, rather than the valence band. In a donor-valence band transition, the initial state is a donor level within the band gap, instead of the conduction band. Again, employing the effective mass approximation and assuming parabolic bands, the emission energy for a band-impurity transition is,

\[
\begin{align*}
\hbar \nu &= E_g - E_a + \frac{h^2k^2}{2m_e} \quad \text{conduction band - acceptor transitions}; \\
\hbar \nu &= E_d - E_v + \frac{h^2k^2}{2m_e} \quad \text{donor - valence band transitions};
\end{align*}
\]  

(2.2 & 2.3)

where \(E_a\) and \(E_d\) represent the acceptor and donor level energies, respectively. Both types of band-impurity transitions are illustrated in (Figures 2.2b and 2.2c).

2.3.2.4 Donor-Acceptor Pair Transitions

Transitions can also occur between donor and acceptor levels giving rise to donor-acceptor (D-A) pair absorption and luminescence as illustrated in Figure 2.2d. A D-A
pair center consists of four particles, two of which are fixed in space with the remaining two being mobile\textsuperscript{22}. In the determination of the recombination energy, it is useful to consider two limiting cases: (i) distant D-A pairs where the separation $R$ of the donor and acceptor ions in the lattice is much larger than the Bohr radius and (ii) associated D-A pairs where $R$ is comparable to the dimensions of either the donor or acceptor ions. For distant D-A pairs, the emission energy is described as,

$$h\nu = E_{d} - (E_{a} + E_{g}) + \frac{e^{2}}{\varepsilon R}$$  \hspace{1cm} (2.4)$$

The donor and acceptor levels are localized in real space, hence, they are extended in k-space\textsuperscript{14}. Consequently, the conservation of momentum law is automatically satisfied. Similarly, for associated D-A pairs, the recombination energy is

$$h\nu = E_{d} - (E_{a} + E_{g}) + \frac{e^{2}}{\varepsilon_{opt} R}$$  \hspace{1cm} (2.5)$$

which differs from Equation (2.4) only in the replacement of $\varepsilon$ by $\varepsilon_{opt}$, the optical dielectric constant. This substitution is appropriate if the orbital frequency of the donor exceeds the longitudinal optical phonon frequency\textsuperscript{23}.
2.3.2.5 Intra-ionic Transitions

In contrast to the inter-ionic transitions of (D-A) pair centers, intra-ionic or localized transitions take place within a single ion or molecule, as is depicted in Figure 2.2e. When the distance between the luminescent centers in a phosphor system is decreased, the excited state of these centers may couple strongly with the vibrations of the lattice. After the termination of excitation, a strong relaxation may occur that brings the luminescent centers out of resonance with their neighbors and thus promotes localization\textsuperscript{34}. Of the types of luminescent processes which have been discussed, intra-ionic transitions are of primary importance for this work.

2.3.3 Sensitized Luminescence

Generally, a phosphor that displays an intra-ionic transition emits radiation that originates from an incorporated center (activator or acceptor) A, within a host crystal lattice. In such a phosphor, the emission initiated in the luminescent center is a result of direct excitation of the activator. However, most activators do not efficiently absorb the high energy VUV (147nm to 172nm) excitation photons utilized in the PDP system. Accordingly, this energy must be absorbed in another center (sensitizer or donor) S, which absorbs well in these regions, and subsequently transfers the energy to the activator. This sensitizer may take the form of either an optically active ion or group of ions within the host lattice\textsuperscript{11}. As inter-ion distances become small enough for optical centers to begin to interact with one another, a single sensitizer ion may relax to the ground state by giving its energy to an activator ion creating internal excitation within the system. This is a non-radiative process and does not involve emission of photons by one
ion and subsequent absorption by the other. Energy transfer depends on a spatial process and can occur over a rather long distance in the lattice (tens to hundreds of lattice planes). It is executed as an excited energy state carried by a phonon wave to the receiving site.

The phonon waves responsible for this energy transfer occur in all systems as the ions in a crystal undergo vibrational oscillations even at 0K (zero point motion). We may describe the oscillation of ions in a crystal through the application of Hooke's law for an elastic vibrator, in which the return force is equal to that of the displacement force so that no energy is lost in the process. We may define Hooke's law as:

$$F = s(\partial u / \partial x) \quad s = (\partial^2 u / \partial x^2) = p(\partial^2 u / \partial t^2) .$$ (2.6)

where \(F\) is the force of displacement, \(t\) is time, \(s\) is a spring constant, \(u\) is a coordinate in the lattice, \(x\) is a lattice direction, and \(p\) is a mass density. These equations may be written in the form of a traveling wave as:

$$u = u_e \exp(-i(\omega t - kx)).$$ (2.7)

in which, \(k = \omega / V_s\) and \(V_s = (s / p)^{1/2}\). The associated energy transfer rate is then,

$$W_{st} = \frac{2\pi}{\hbar} \left| \langle S, \hat{A} | H_{st} | S^*, \hat{A} \rangle \right|^2 \int \langle \tilde{E} \rangle g_s(\tilde{E}) g_t \tilde{E} d\tilde{E} .$$ (2.8)
in which \( \hbar \) is Planck's constant over \( 2\pi \) and \( H_0 \) is a Hamiltonian operator describing the energy overlap. The variables of \( S/S^* \) and \( A/A^* \) are the ground/excited states of the sensitizer and activator ions, respectively. The Hamiltonian operator can be either the Coulomb force between the two ions, or the exchange interaction, which depends on the physical overlap of electronic wavefunctions\(^1\). This Coulomb interaction can be further refined to dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, etc. In all cases, the energy transfer rate is directly proportional to the overlap integral,

\[
\int \langle E \rangle g_1(E) g_2 dE.
\]

(2.9)

Accordingly, the process is most efficient between two ions with similar energy level structures in which a resonant energy transfer is observed\(^1\).

This energy transfer process may be extended to the non-resonant case in which a large mismatch in the energy levels of the ions exists. This is the case encountered in a typical blue component PDP phosphor in which the excited states at 147nm present no overlapping wavefunctions with the emitting states in the visible region of 450nm. Energy transfer may occur through coupling of each state to the lattice via phonon exchange. This involves emission of a virtual phonon from the excited state of an anion group to the lattice, which is immediately followed by absorption at the activator site with simultaneous spatial transfer of resonant energy by an allowed multipole process. In other words, two mismatched multipoles can readjust their energy states so that a resonant energy transfer process can occur. We simply include phonon processes as part
of the energy transfer process integral given above as phonons are created to satisfy the energy conservation principle.

Figure 2.3 displays the processes of both resonant and non-resonant energy transfer. In each case, $b_1^-$ and $b_1^+$ are the annihilation and creation operators of energy states within the sensitizer (single or ion group) and activators, respectively. The creation of a phonon is denoted by $c^+$. Furthermore, to distinguish the act of donating and accepting the energy with the simultaneous change of the atomic states, single solid (down) and double solid (up) lines are used, respectively. Phonon creation is displayed with a single dashed (up) line.\cite{25}
Figure 2.3: Illustration of non-radiative processes of energy transfer, where \( b_i \) and \( b_i^* \) are the annihilation and creation operators of energy states and \( c^* \) denotes the creation of a phonon.
The issue regarding the probability of efficient energy transfer from the sensitizer was addressed by Dexter, in 1953. His work suggests that the distance $R$ between centers and the probability of a transfer from S to A, $(P_{SA})$, are related. The distance for which $P_{SA}$ (transfer rate) = $P$ (radiative and nonradiative internal decay rate) is called the critical distance $R_C$. If $R > R_C$, radiative emission from S will likely take place, while when $R < R_C$, energy transfer from S to A dominates. However, a high value of $P_{SA}$ does not ensure the occurrence of transfer since the excited state of S (i.e., $S^*$) may have alternate decay paths either radiatively ($P_r$) or non-radiatively ($P_{nr}$). Thus, transfer can only occur if $P_{SA} > P_r + P_{nr}$.

2.3.4 Lattice Interactions

It is expected that local phonon modes around an activator site will differ from those of the lattice phonon waves due to a difference in the mass of the activator cation relative to those cations of the host lattice. Accordingly, there is a set of local phonon modes surrounding the impurity activator site, which displays an upper cutoff frequency. Considering this localization behavior, it is preferable to treat the optical excitations or emissions with a localized mode. This is best accomplished by the configurational coordinate model (CCM), which is often used to describe transitions between electronic energy levels coupled to lattice vibrations. In the general case, ions are approximated as simple harmonic oscillators in a normal mode coordinate system. The normal modes of the distortion of a complex consisting of an activator with six neighboring ions (octahedral symmetry) are illustrated in Figure 2.4.
Figure 2.4: Vibrational modes of the lattice in a solid.
Consider the absorption and emission processes in Figure 2.5, which consists of two energy curves representing the ground and excited states with associated lattice vibrations. If the breathing mode (A1g) of Figure 2.4 is taken as the vibrational mode for the lattice, the distance from an activator to neighboring ligand ions is called the configurational coordinate $Q$ for the system$^{11,12}$. The equilibrium position for the ground state is labeled $Q_0$ while the equilibrium position for the excited state is labeled $Q_e$. The equilibrium positions of the configuration coordinate are different for the ground and excited states due to the difference in the electron-lattice coupling in the two states. When sufficient energy is absorbed, an electronic transition from the ground to excited state ($a \rightarrow b$) of the activator center occurs (Figure 2.5)$^{12}$. According to the Frank-Condon principle, this transition occurs in a time nearly instantaneous, as compared to relaxation (phonon) processes within the activator center. Accordingly, the optical transitions of the configuration coordinate diagram are represented by vertical lines. To understand why this is so, we must again consider the energy interactions that occur when a photon strikes a solid in which the timeframe of interaction is about $10^{-18}$ seconds.

\[
\text{Speed of photon} = v = 10^8 \text{ cm/sec}
\]

\[
\text{Distance between typical lattice planes} = d = 10^{-8} \text{ cm}
\]

\[
\text{Time for photon to traverse lattice plane} = d/v = 10^{-18} \text{ seconds}
\]
Figure 2.5: Configurational coordinate diagram for a simplified two-level system.
The vibrational modes of the excited activator are somewhat different than those of the ground state yet remain strongly coupled\(^1\). This is known as vibronic coupling and is caused by phonon wave propagation throughout the host lattice, and interaction at the activator center. Recall that unless the host lattice is at 0K, vibrational waves are always present. Consequently, there may be several excited states possible and whether upper states are involved depends only upon the original energy of the exciting photon\(^1\). This energy may exceed the minimum energy required for excitation and consequently, excess energy may cause upper states to become populated. Therefore, once the activator center has become excited, it must typically relax through several excited phonon levels until it reaches the lowest energy excited state (position c in Figure 2.5) from which radiative emission may occur (c \(\rightarrow\) d)\(^2\).

This process, results in a density of states arising from the random action of phonon perturbation of the excited state, both before it relaxes and afterwards. It is this random formation of Gaussian energy states that gives rise to a broad band in both the excitation and emission spectra of the Eu\(^{3+}\) activator ion. If both host and activator center were cooled to 0K, the electronic transition would then be between a single phonon level of the ground state to a single level in the excited state. This would result in essentially a single energy line known as the "zero-phonon line". As the temperature rises, increased phonon wave branching intensities result and the emission band is broadened.\(^1\) As relaxation occurs in the excited state, a shift in the configurational coordinate Q occurs. If this shift in the emission peak as compared to the absorption peak is to longer wavelengths (lower energy), the magnitude is referred to as the Stokes shift (Figure 2.6).
Figure 2.6: Idealized absorption and emission spectra of a two-level system subject to electron-phonon interactions.
2.3.5 Crystal Field Theory

The energy levels and optical transitions of ions in a solid can be specifically assigned by extending the configurational coordinate model using crystal field theory\textsuperscript{35,34}. Crystal field theory treats a metal ion in a complex molecule or crystal as if it were subject to a purely electrostatic perturbation by its surroundings\textsuperscript{35}. When a free ion is placed into a crystal, either substitutionally or interstitially, it is perturbed by interaction with ligand ions and this may result in a splitting of the free ion energy levels. In the crystal field approximation, ligand ions are treated as point charges and their effect on valence electrons are described only by Coulomb interactions. Fundamentally, the energy level splitting within such a field is due to a primary reduction in the rotational symmetry of the affected free ion\textsuperscript{16}. Hence, it is possible to simplify the problem based solely on symmetry properties of the system under consideration.

Optical transitions usually involve valence electrons, while the inner electrons are normally unaffected. In this case, termed the central field approximation, the inner electrons contribute to an overall averaged field. In the case of a transition metal activator ion, the Coulomb interaction and crystal field are the dominant forces and thus any spin-orbit interaction can be treated as a small perturbation\textsuperscript{14}. For rare earth ions, the \textit{f}-electrons are partially screened from the crystal field by the outer shell electrons and the spin-orbit interaction becomes the dominant force along with Coulomb interactions. Accordingly, the crystal field may be treated as a small perturbation\textsuperscript{14}. If however, a rare earth ion loses this screening due to a reduction of the valence state as is found in Eu\textsuperscript{2+}, the crystal field perturbation again becomes a dominating factor.
2.4 Luminescence Characteristics of Eu$^{2+}$

Activators such as divalent europium, Eu$^{2+}$, are categorized as inter-configurational in nature$^{37}$. Depending upon covalency and the strength of the crystal field environment it is placed within, the emission of Eu$^{2+}$ can vary from long-wavelength ultraviolet to yellow. As a result of this optical property, Eu$^{2+}$ is considered a very useful activator for display applications. The electron configuration of Eu$^{2+}$ is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^{10}\,5s^2\,5p^6$, and displays luminescence due to the parity-allowed electric dipole $4f^75d^1 \rightarrow 4f^{10}$ transition$^{38}$. The electronic configuration of the Eu$^{2+}$ ground state is $4f^7$ with $^8S_{7/2}$ as the lowest term. When there is no external field, the $d$-electron can occupy any of the 5 orbitals which are degenerate. However, if this ion is placed in a crystal with octahedral symmetry, one of the 4f electrons is promoted to a 5d level and the remaining six are left behind in the lower 4f configuration where they are shielded by outer shell electrons. This results in a deformation of the electronic wavefunctions which causes energy levels to be changed, resulting in a splitting of the 5d orbitals into $e_g$ and $t_{2g}$ orbitals which are doubly and triply degenerate, respectively$^{22}$. Only the 5d-electron can then be influenced and it is this characteristic, which results in the high sensitivity of Eu$^{2+}$ to crystal field perturbation and energy transfer efficiency.

Figure 2.8, shows the angular dependence of the 5 d-orbitals in an octahedral crystalline environment in which the 3 orbitals labeled $\phi(t_2)$ possess the same symmetry and are thus, indistinguishable. These orbitals are degenerate and correspond to the 3-fold $t_{2g}$ level obtained above using group theoretical arguments. The remaining 2, labeled $\phi(e)$, are clearly distinguishable from the $\phi(t_2)$ orbitals and form the 2-fold degenerate $e_g$ level.
Due to a larger degree of overlap with neighboring ions, the doubly degenerate level has the higher energy\textsuperscript{22}. The ligand field strength is reflected by the energy difference, $\Delta D_Q$, between the $e_g$ and $t_{2g}$ orbitals of the 5d configuration and is referred to as the crystal field strength (Figure 2.7). This parameter has a dependence on bond length, ion charge, and ion radius as follows,

$$\Delta D_Q = \frac{Ze^2}{6a^2} \left\{r^4\right\}$$ \hspace{1cm} (2.10)

Accordingly, the emission properties of Eu\textsuperscript{3+} are expected to vary with the size and crystallinity of the pyrophosphate host lattice it is placed within.
Figure 2.7: Energy level splitting of the excited state in Eu$^{3+}$ under the influence of an octahedral crystal field.
2.5 The Role of Phosphors in PDP Technology

2.5.1 Introduction

An understanding of the role that phosphors play in color display technology requires an examination of the response of the human eye to color. Visible light constitutes only a small part of the electromagnetic spectrum and the portion perceived by the human eye covers a fairly narrow band from 380nm to 780nm\(^1\). Not all human eyes react the same, so a quantitative method for describing color is necessary and can be achieved by testing the perception of many individuals and averaging the results. This average is termed the standard observer and allows for the production of a luminosity curve, which yields a spectral sensitivity plot of the human eye (Figure 2.8). The brightest part of the spectrum in the photopic range (vision under high levels of illumination) occurs near 555nm, in the green-yellow region. Under low levels of illumination, or the scotopic range, the region of highest response is near 510nm, in the blue-green region of the spectrum\(^2\). This variation in spectral response under different illumination levels arises from the distinct receptors in the human eye; cones are responsible for photopic vision and rods are responsible for scotopic. These receptors are approximately red, green, and blue. It is found that the eye acts as an integrating instrument and thus, two colors may appear equal to the eye even though one is monochromatic light and the other has a band of wavelengths\(^3\). Accordingly, we may see the same color, even though the photon energies are much different.
Figure 2.8: Luminosity curves for the standard observer. The peak of the scotopic (low level) is in the Blue-Green region and that of the photopic (high level) is in the Green-Yellow region.
2.5.2 The Quantification of Color

Using a glass prism in combination with slits, Sir Isaac Newton first demonstrated that sunlight consisted of colors. Subsequent work showed that colors could be duplicated by mixing the three primaries of red, green, and blue to obtain various hues, including shades of white. Color perceived from a self-emitting object is typically described by its hue, brightness, and saturation. Hue is the attribute that we denote by red, yellow, or green and is determined by the dominant wavelength. The degree to which a color differs from white describes its saturation and provides a description of the purity of chromaticity. Finally, brightness or luminance is the attribute used to describe the perceived intensity of light\textsuperscript{43}.

These attributes describe color in a qualitative manner. For scientific purposes, a quantitative method of describing color is necessary. To do this, the CIE system developed by the Commission Internationale de l’Eclairage (International Commission on Illumination) is used. It is based on trichromatic theory and deals with three fundamental aspects of color – the object, the light source, and the observer\textsuperscript{44}. A set of tristimulus values (X, Y, Z), are used to denote the intensities of the colors in any arbitrary sample spectra. Although it is a simplified way of thinking of the tristimulus values, one may view these as the amount of red, green, and blue in a sample. The tristimulus values X, Y, Z can be calculated by using the color matching functions given in Figure 2.9.
Figure 2.9: Color matching functions for the CIE standard observer.
As noted previously, these functions have been derived by determining the average response of the human eye. Each tristimulus value for a sample of interest is calculated by integrating the product of the power output of the sample and the color matching function:

\[
X = \int S(\lambda) \cdot x(\lambda) \cdot d\lambda.
\]

\[
Y = \int S(\lambda) \cdot y(\lambda) \cdot d\lambda.
\]

\[
Z = \int S(\lambda) \cdot z(\lambda) \cdot d\lambda.
\]  

(2.11 a,b,c)

Chromaticity coordinates \(x\), \(y\), and \(z\) are then derived by normalizing each of the tristimulus values as follows.

\[
x = \frac{X}{X + Y + Z}, \quad y = \frac{Y}{X + Y + Z}, \quad z = \frac{Z}{X + Y + Z}.
\]  

(2.12 a,b,c)

Since the sum of \(x\), \(y\), and \(z\) must equal 1, we need only consider the pair \((x, y)\) which is commonly plotted on a CIE chromaticity diagram which gives a quantitative value of color (Figure 2.10). Colors with chromaticity coordinates near the perimeter of the diagram are regarded as being saturated whereas, true white light has equivalent chromaticity coordinates, i.e. \(x = y = 0.33^{\text{at}}\).

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Figure 2.10: CIE Chromaticity diagram. The triangle represents the CIE coordinates for the P22 CRT phosphor set.
2.5.3 Application to the Plasma Display Panel

On the basis of the triphosphor system, the chromaticity requirements for each phosphor have been determined, and are summarized in Table 2.1. In addition to the required CIE coordinates, the intensities of blue, green, and red must be in the ratio of 1:6:3 in order to achieve a balanced white.

Table 2.1: CIE Coordinates for phosphors in a tri-chromatic system

<table>
<thead>
<tr>
<th>CIE coordinate</th>
<th>Red</th>
<th>Green</th>
<th>Blue</th>
<th>White</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>&gt; 0.55</td>
<td>&lt; 0.30</td>
<td>&lt; 0.15</td>
<td>= 0.33</td>
</tr>
<tr>
<td>y</td>
<td>&lt; 0.30</td>
<td>&gt; 0.50</td>
<td>&lt; 0.15</td>
<td>= 0.33</td>
</tr>
</tbody>
</table>

The full color capability of the PDP is made possible through an arrangement of red, green, and blue (RGB) picture elements commonly known as pixels. Each pixel is a tiny gas-discharge cell, which either radiates visible light directly or emits the luminescence produced by phosphors (Figure 2.11). Photoluminescence from the combination of these pixels is the mechanism that produces the many colors or hues observed in the modern PDP system.

The discharge gap of the RGB cells (sub pixels) is on the order of a few hundred micrometers and the minimum firing voltage of 200 volts requires gas pressures of several hundred Torr. Therefore, the low pressure of mercury discharge (10⁻³ Torr at room temperature) typically used in fluorescent lamps is not suitable for the excitation of
Figure 2.11: Illustration of an AC drive Plasma Display Panel (PDP).
PDP phosphors\(^{45}\). Potential discharge gases must have high radiation intensity characteristics, be chemically stable, and exhibit a weak visible emission in order prevent degradation of color purity character. The combinations of discharge gas most widely used in PDPs are mixtures of Xe-He or Xe-Ar\(^{46,47,48}\). Under the influence of an electric field, the Xe gas discharge results in an intense VUV photon resonance line at 147nm and a secondary line at 172nm which is significantly lower in intensity. The addition of the buffer gases to Xe is used to increase the pressure and ensure a longer panel life\(^{49}\).

Criteria for the design of PDP phosphors include stability under VUV radiation and ion bombardment, high band-gap, and high quantum efficiency under excitation in the vacuum ultraviolet, 147nm and above. Table 2.2, shows a list of typical combinations of tricolor phosphors that have been used in PDP systems\(^{49}\).

Table 2.2: Combinations of the tricolor phosphors that have been used in PDPs.

<table>
<thead>
<tr>
<th>Set Number</th>
<th>Red (R)</th>
<th>Green (G)</th>
<th>Blue (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CaWO(_4)</td>
<td>Zn(_2)SiO(_4):Mn(^{2+})</td>
<td>Y(_2)O(_3):Eu(^{3+})</td>
</tr>
<tr>
<td>2</td>
<td>Y(_2)SiO(_5):Ce(^{3+})</td>
<td>Zn(_2)SiO(_4):Mn(^{2+})</td>
<td>Y(_2)O(_3):Eu(^{3+})</td>
</tr>
<tr>
<td>3</td>
<td>Y(_2)O(_3)V(_2)O(_5):Eu(^{3+})</td>
<td>Zn(_2)SiO(_4):Mn(^{2+})</td>
<td>Y(_2)O(_3)V(_3)O(_5):Eu(^{3+})</td>
</tr>
<tr>
<td>4</td>
<td>BaMg(_2)Al(_2)O(_4):Eu(^{2+})</td>
<td>Zn(_2)SiO(_4):Mn(^{2+})</td>
<td>Y(_2)O(_3):Eu(^{3+})</td>
</tr>
<tr>
<td>5</td>
<td>BaMg(_2)Al(_2)O(_4):Eu(^{2+})</td>
<td>Zn(_2)SiO(_4):Mn(^{2+})</td>
<td>Y(<em>{0.65})Gd(</em>{0.35})BO(_3):Eu(^{3+})</td>
</tr>
<tr>
<td>6</td>
<td>BaMg(_2)Al(_2)O(_4):Eu(^{2+})</td>
<td>BaAl(_2)O(_3):Mn(^{2+})</td>
<td>Y(<em>{0.65})Gd(</em>{0.35})BO(_3):Eu(^{3+})</td>
</tr>
</tbody>
</table>
Among the phosphors listed in Table 2.2, the combination that has been most widely used in PDPs is that which combines (Y,Gd)BO$_3$:Eu$^{3+}$ (Red), BaAl$_2$O$_3$:Mn$^{2+}$ (Green), and BaMgAl$_4$O$_{19}$:Eu$^{2+}$ (Blue). The advantages of this combination are:

1. the highest conversion efficiency of VUV radiation into visible emission;
2. wide reproducible color gamut;
3. white color representation at equal discharge currents; and
4. no serious damage to other panel characteristics.

The most significant problems of this RGB set are color purity (Red), decay time (Green), and degradation (Blue).
2.6 Characteristics of the alkaline earth pyrophosphates

Alkaline earth pyrophosphates of the form $X_2Y_2O_7$ are polymorphic in nature and belong to a small number of related structure groups. Crystals for which the ionic radius of the X ion is greater than 0.97Å, crystallize in a series of related structures known as dichromates\(^{39}\). The X atom is a large alkaline earth such as Ca, Sr, or Ba. The Y atom is a member of group V or VI of the periodic table such as P, V, S, or Cr\(^{39}\). The crystals can therefore be viewed as ionic where $X^{2+}$ is the cation and $(Y_2O_7)^{4-}$ is the anion. In this structure, the $(Y_2O_7)^{4-}$ ion consists of two YO$_4$ tetrahedra sharing an oxygen atom with a Y-O-Y angle of approximately 130° (Figure 2.12a). This anion occurs in an eclipsed configuration in the dichromate structure where the bridging oxygen atom lies almost on the line joining two of the terminal oxygen atoms. These three oxygen atoms are referred to as the backbone and the remaining four oxygen atoms, which are nearly co-planar with each other, are referred to as the feet\(^{19}\). The cations lie close to the plane of the feet. Most of the dichromate structures are built out of sheets which are generated from the basic ion unit by two translation vectors (i) and (k). The (i) vector lies in the plane of the feet and allows molecules to arrange next to each other. The (k) vector is perpendicular to the backbone and allows each sheet to stack one upon another. There are two luminescent phases of interest, beta and alpha (Figure 2.12b).
Figure 2.12. Crystal structures of $(P_2O_7)^-$ in (a) and $(Ca,Sr)_2P_2O_7$:Eu in (b)
The structural difference between the two is subtle and involves a rotation about an axis along the (k) vector. In the beta-phase, the backbones are positioned at 60° to the (i) vector. The transition to the alpha-phase is a simple progression of this angle from 60° to 90° to the (i) vector and occurs at different temperatures depending on which cation is found in the molecule. The firing temperature required to change from one form to the other (with differing crystal structure) varies from 1150°C for Ca-based to 750°C for Sr-based\textsuperscript{10}. The crystal structure factors of the complete pyrophosphate series are presented in Table 2.3, in which a clear distinction can be made between the crystal field environment of the β and α phases. The α phase provides an octahedral coordination environment for Eu\textsuperscript{3+} activators whereas the β phase displays a mixed coordination system. It is this characteristic of the β phase that precludes its use as an efficient host lattice structure\textsuperscript{11}.

Table 2.3: Structure and metal cation coordination properties for the pyrophosphates.

<table>
<thead>
<tr>
<th>Phase &amp; Temp.</th>
<th>Crystal Structure</th>
<th>Lattice Symmetry</th>
<th>Cation Coordination</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-Ca\textsubscript{3}P\textsubscript{2}O\textsubscript{7} (LT)</td>
<td>Tetragonal</td>
<td>C\textsubscript{4v} (P4\textsubscript{1})</td>
<td>7,8,9 oxygens</td>
</tr>
<tr>
<td>β-Sr\textsubscript{3}P\textsubscript{2}O\textsubscript{7} (LT)</td>
<td>Tetragonal</td>
<td>C\textsubscript{4v} (P4\textsubscript{1})</td>
<td>7,8,9 oxygens</td>
</tr>
<tr>
<td>α-Ba\textsubscript{3}P\textsubscript{2}O\textsubscript{7} (LT)</td>
<td>Orthorhombic</td>
<td>C\textsubscript{2v} (Pna2\textsubscript{1})</td>
<td>6 oxygens</td>
</tr>
<tr>
<td>α-Ca\textsubscript{3}P\textsubscript{2}O\textsubscript{7} (HT)</td>
<td>Orthorhombic</td>
<td>C\textsubscript{2v} (Pna2\textsubscript{1})</td>
<td>6 oxygens</td>
</tr>
<tr>
<td>α-Sr\textsubscript{3}P\textsubscript{2}O\textsubscript{7} (HT)</td>
<td>Orthorhombic</td>
<td>C\textsubscript{2v} (Pna2\textsubscript{1})</td>
<td>6 oxygens</td>
</tr>
<tr>
<td>δ-Ba\textsubscript{3}P\textsubscript{2}O\textsubscript{7} (HT)</td>
<td>NOT KNOWN</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

41
The alpha forms are orthorhombic, with the following lattice parameters in Angstroms\(^{40}\):

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(_2)P(_2)O(_7)</td>
<td>8.44</td>
<td>12.52</td>
<td>5.26</td>
</tr>
<tr>
<td>Sr(_2)P(_2)O(_7)</td>
<td>8.87</td>
<td>13.27</td>
<td>5.39</td>
</tr>
<tr>
<td>Ba(_2)P(_2)O(_7)</td>
<td>9.35</td>
<td>13.87</td>
<td>5.61</td>
</tr>
</tbody>
</table>

The Ca\(_2\)xSr\(_{x-x}\)P\(_2\)O\(_7\);Eu\(^{3+}\) (x = 0 to 2) composition range in which is a classic example of a substitutional solid solution, i.e. one in which chemical variation is achieved by substitution of one type of atom in the structure for another. In general, if the size difference between the cations is less than 15%, a solid solution is often very extensive or complete. As the radius of Ca and Sr ions (0.99 and 1.13 Angstroms) are within a 14% difference and each display the same bonding characteristics in the pyrophosphate lattice, the α-phase solid solution is found to be very nearly ideal. This may be best understood within the context of the measure of excess enthalpy throughout the Ca\(_2\)xSr\(_{x-x}\)P\(_2\)O\(_7\);Eu solid-solution range. The excess enthalpy is defined relative to a mechanical mixture of the two end-members of Ca and Sr-pyrophosphate as the enthalpy of mixing (ΔH). The mathematical form of the enthalpy of mixing can be derived using a simple model, assuming the energy of the solid solution arises only from the interaction between nearest-neighbor ion pairs\(^{41}\). If the total number of lattice sites is \(N\) and the coordination number of these on which mixing occurs is \(z\), then the total number of nearest neighbor bonds is \(1/2Nz\) as the number of bonds is half the number of sites. The energy associated with Ca-Ca, Sr-Sr, and Ca-Sr nearest neighbor pairs is \(W_{CaCa}\), \(W_{SrSr}\), and \(W_{CaSr}\), respectively. If cations are mixed randomly, the probability of Ca-Ca, Sr-Sr, and Ca-Sr
neighbors is \(x_{\text{Ca}}^2\), \(x_{\text{Sr}}^2\), and \(2x_{\text{Ca}}x_{\text{Sr}}\), respectively. The total enthalpy of the solid solution is then:

\[
H = \frac{1}{2} N \left( x_{\text{Ca}}^2 W_{\text{CaCa}} + x_{\text{Sr}}^2 W_{\text{SrSr}} + 2x_{\text{Ca}}x_{\text{Sr}} W_{\text{CaSr}} \right) .
\]  

(2.13)

which simplifies to:

\[
H = \frac{1}{2} N \left( x_{\text{Ca}} W_{\text{CaCa}} + x_{\text{Sr}} W_{\text{SrSr}} \right) + \frac{1}{2} N \left[ x_{\text{Ca}} x_{\text{Sr}} \left( 2W_{\text{CaSr}} - W_{\text{CaCa}} - W_{\text{SrSr}} \right) \right] .
\]  

(2.14)

The first term in equation 2.14 is the enthalpy of the mechanical mixture. The second term is therefore the enthalpy of mixing:

\[
\Delta H_{\text{mix}} = \frac{1}{2} N \left[ x_{\text{Ca}} x_{\text{Sr}} \left( 2W_{\text{CaSr}} - W_{\text{CaCa}} - W_{\text{SrSr}} \right) \right] = \frac{1}{2} N x_{\text{Ca}} x_{\text{Sr}} W .
\]

(2.15)

in which \(W\)'s are referred to as the regular solution interaction parameters\(^{11}\). The sign of \(W\) determines the sign of the enthalpy of mixing. The effects of enthalpy variation are shown in Figure 2.13. If it is energetically more favorable to have Ca-Ca and Sr-Sr neighbors rather than Ca-Sr neighbors, then \(W\) is positive and the solid solution will attempt to maximize the number of Ca-Ca and Sr-Sr neighbors by segregating into Ca-rich and Sr-rich regions and is referred to as exsolution. If it is energetically more favorable to have Ca-Sr neighbors rather than Ca-Ca and Sr-Sr neighbors, then \(W\) is negative and the solid solution will attempt to maximize the number of Ca-Sr neighbors by forming an ordered compound which is referred to as cation ordering\(^{11}\).
Figure 2.13: Effects of variation in enthalpy within a solid solution of A and B ions.
Due to the larger radius of the Ba$^{2+}$ (1.35) ion relative to Ca$^{2+}$ (0.99) and Sr$^{2+}$ (1.13), no solid-solution of Ba$_3$P$_2$O$_7$ can be formed with either Ca$_3$P$_2$O$_7$ or Sr$_3$P$_2$O$_7$ within the α-phase. Very little substitution of Ba for Ca or Sr ions will occur and thus, miscibility may be limited to low concentrations only$^{42}$. Consequently, a miscibility gap is observed at intermediate compositions (Figure 2.14).
Figure 2.14: Complete pyrophosphate range consisting of Ca, Sr, and Ba cations indicating a miscibility gap formation with Ba inclusion.
2.7 The Solid-State Reaction Technique

As the goal of this research was to determine the fundamental ability of the pyrophosphates to be applied as a blue component PDP phosphor, a large number of samples were required to elucidate any luminescent trends present in the Ca$_2$Sr$_2$P$_2$O$_7$:Eu system. The solid-state reaction (SSR) technique was chosen as it enables the relatively rapid production of samples and is currently the synthesis method of choice in the phosphor industry. However, the SSR technique is not without difficulties, and can therefore pose significant challenges to the production of highly sensitive functional materials as required for PDP applications. In general, we may classify solid state reactions as being either homogeneous or heterogeneous. The former involves reactions within a single compound whereas the latter involves reactions between two different compounds. Thermodynamic and kinetic factors are important in heterogeneous solid state reactions: thermodynamic considerations show whether or not a particular reaction should occur by considering the changes in free energy that are involved; kinetic factors determine the rate at which the reaction occurs.$^{51-54}$

Consider the heterogeneous solid state reaction between two species, (A) and (B). At the moment of “joining” (A and B), the “activated complex” is formed as illustrated in Figure 2.15. The free energy of the activated complex, $G^*$, is higher than that of the initial state. If the equilibrium constant of the activated complex is represented by $K^*$, the change in free energy may be written as,

$$\Delta G = RT \ln K^*. \quad (2.16)$$
where the (*) refers to the activated species. We may use $x_{dt}$ as a radius to define a
growth rate and $N$ as the number of nuclei formed in $(t-y)$ time. Accordingly, it is
shown that the volume $V$ formed as a function of that time will be:

$$V(t) = \int \left\{ g \left[ x_{dt} \right]^2 \left( \frac{dN}{dt} \right)_{x_{dt}} \right\} \, dy.$$  \hspace{1cm} (2.17)

where the $g$ term is a geometrical shape factor$^{11}$. In general, the rate of solid state
nucleation is similar to the reaction rate of the species. Rate processes are defined in
terms of a rate, $r$, and a volume $V$, usually a molar volume. Thus we have for the
heterogeneous case:

$$r = \frac{1}{V(t)} \left( dV \right) \left/ d t \right.$$. \hspace{1cm} (2.18)

where $V_t$ is the volume at time, $t$, and $V_f$ the final volume. Thus the fraction
decomposed at any time, $t$, is:

$$x = \frac{V_t}{V_f}.$$ \hspace{1cm} (2.19)
Figure 2.15: Variation in free energy associated with formation of the activated complex of AB atoms during a solid-state reaction process.
The critical obstacle in the formation and growth of nuclei in solid state reactions is the extremely slow diffusion rate of most solids. It is typically observed that very high annealing temperatures are generally required to drive the diffusion in a reasonable period of time. Unfortunately, these high annealing temperatures may provide sufficient energy to nucleate any number of crystalline phases at reacting interfaces. This type of scenario offers very little opportunity to examine the precise mechanism of a reaction due to the fact that the process is diffusion limited, and may pass through many stable intermediate phases before completion. The overall solid state reaction is dependent upon the rate of diffusion of each species involved and these rates are often very different. This is due to the fact that a particular phase (AB), has a certain ordered structure and each species, (A) and (B), is required to move through this structure to reaction boundaries. A given A-atom displaces one of the A-atoms in (AB) and this displaced A-atom then causes another displacement by a “hopping” motion. The stated displacement then continues until the other phase boundary is encountered where reaction of the final displaced A-atom occurs with a B-atom to form (AB). Simultaneously, the walls of (AB) move in a three-dimensional direction at the expense of both volumes of (A) and (B). The ability of (A) or (B) atoms to move or diffuse through the (AB) phase greatly depends on their respective electronic properties and the reaction control mechanisms at work.

Simple-diffusion and phase-boundary controlled mechanisms are of particular importance in this work. Simple diffusion-controlled reactions may be described by,

\[ X^2 = 2D c_0 t V_M + (a)^2 \]  \hspace{1cm} (2.20)
in which \(c_0\) = concentration of constituents at the interface of (A) to (AB); \(V\) = volume of product (AB) per mol of reactants; \(a\) = surface layer thickness at interface when \(t = 0\). It is also well to note that the final volume of the product, (AB), may not be the same as that of the reactants.

We may consider a more practical example involving diffusion and reactivity, such as the reaction between particles of CaO and SiO\(_2\). This solid state reaction is very slow, even at 800°C, and occurs at the interface of the two types of particles\(^{11}\).

\[
2(\text{CaO}) + \text{SiO}_2 \rightarrow \text{Ca}_2\text{SiO}_4
\]

(2.21)

The reaction is slow because it is diffusion-limited. Due to the three-dimensionally bound nature of the silica network, reaction occurs by the diffusion of Ca\(^{2+}\) atoms within the network and progresses only in one direction since the silica-tetrahedra are not free to move. The three-dimensional network of tetrahedra is being rearranged to form another structure. Although the general rate of diffusion is controlled by the nature of the lattice structure, diffusion by cations typically prevails in oxygen-dominated hosts\(^{11}\).

For phase-boundary controlled reactions, the situation is somewhat different. Diffusion of species is relatively fast but the reaction is slow which causes diffusing species to pile up. That is, the reaction to rearrange the structure is slow in relation to the arrival of diffusing ions or atoms. Thus, a phase-boundary or difference in structure is present which controls the overall rate of solid state reaction which may be described by:

\[
\frac{dx}{dt} = k_1 \left( \frac{s_i}{V_a} \right) \rightarrow 1 - (1-x)^n = k_1 t x = \frac{dx}{dt}
\]

(2.22)
in which \( x = \) instantaneous surface area; \( V_o = \) original volume of particles reacting; \( r_o = \) original radius of particles; and \( n = 1, 1/2, 1/3 \) for a 1-, 2-, or 3-dimensional reaction\(^{11}\).

Turning again to our example, let us now suppose that further reaction takes place at the phase boundary of CaO and Ca\(_2\)Si\(_2\)O\(_6\), and also at Ca\(_3\)Si\(_2\)O\(_4\) and SiO\(_2\). If we call these new phases X and Y, it would initially appear that X should be Ca\(_2\)SiO\(_3\) and Y should appear as Ca\(_3\)Si\(_2\)O\(_7\). Consultation of the phase diagram of this system indicates that the former stoichiometry does not exist, but the latter does\(^{11}\). Therefore, the diffusing species, Ca\(^{2+}\) and O\(^{-}\), continue to diffuse until they reach the vicinity of the pyrosilicate, Ca\(_3\)Si\(_2\)O\(_7\), where reaction at the phase boundary is:

\[
\text{Ca}^{2+} + \text{O}^- + \text{Ca}_2\text{Si}_2\text{O}_3 \rightarrow 2 \text{Ca}_3\text{Si}_2\text{O}_6.
\] (2.23)

There is nothing to stop the further diffusion of these species and they therefore, continue to diffuse to the vicinity of the SiO\(_2\) phase boundary, where the reaction is:

\[
\text{Ca}^{2+} + \text{O}^- + \text{SiO}_2 \rightarrow \text{CaSiO}_3.
\] (2.24)

In the opposite direction, diffusion leads to:

\[
\text{Si}^{4+} + 2\text{O}^- + \text{Ca}_3\text{Si}_2\text{O}_7 \rightarrow 3 \text{CaSiO}_3.
\] (2.25)

The overall reaction is that which forms the metasilicate stoichiometry (Figure 2.16)\(^{11}\).
Figure 2.16: Progression of the solid-state reaction between CaO and SiO₂ that leads to formation of a mixed structure.
In the sequence of diffusion reactions, we note that Ca$_2$SiO$_4$ is formed immediately, followed by Ca$_3$Si$_2$O$_7$. Both start to disappear when CaSiO$_3$ begins to form. Near the end, CaSiO$_3$ becomes the major phase present, but the system never reaches the point where just one compound remains. It is observed that a mixture is always obtained and this leads to the general case that reactions between refractory oxides, which are diffusion-controlled, always result in a mixture of compounds$^{11}$. 

To evade this situation, a super-reactive constituent species may be used to bypass the dependence of the solid state reaction upon diffusion and to obtain 100% of the desired product$^{11}$. A typical example is found in CaCO$_3$ which decomposes via,

$$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2.$$ \hspace{1cm} (2.26)

The CaO particles so produced are very small and therefore, have an extremely large surface area. This enables the solid state reaction to occur in a manner that effectively bypasses any diffusion limits and provides for the following reaction,

$$2(\text{CaCO}_3) + \text{SiO}_2 \rightarrow \text{Ca}_3\text{SiO}_4 + 2(\text{CO}_2).$$ \hspace{1cm} (2.27)

In the case of an oxide constituent such as CaO, the number of nuclei formed per unit of time is relatively small and structure formation is diffusion limited. However, when a reactive constituent such as CaCO$_3$ is utilized, the number of nuclei formed per unit of time is increased by many orders of magnitude and structure formation occurs at a rate almost equal to the speed of CaO production.
CHAPTER 3
EXPERIMENTAL PROCEDURE

3.1 Introduction

Phosphors are a highly sensitive class of functional material that are influenced by a number of factors. The extent to which structure-property relations are effected by material synthesis technique depends in part on the type of energy transition mechanisms at work in a particular phosphor material. In many respects, the PDP phosphor may be viewed as an extreme case due to the multiple roles played by the host lattice. This structure is responsible for both the absorption of VUV photons and the subsequent transfer of resulting excitation energy to activator sites. As these actions involve the ability of the lattice to promote efficient energy transfer through the resonance of phonon waves, the importance of phase purity and overall crystallinity cannot be overstated. These host lattice characteristics are also directly responsible for the incorporation of activator ions within the proper crystal field environment. This is particularly important in the case of the Eu$^{2+}$ ion utilized in this study due to the high degree of crystal field sensitivity displayed by its’ unshielded valence electrons. Further, the presence of even minor quantities (100 ppm) of an impurity may lead to energy traps known as “killer centers” that create pathways for non-radiative relaxation of excited activator states$^{11}$. Additionally, the surface morphology of these phosphor systems is a key variable in luminescent performance due to the short absorption length of incident VUV radiation. Thus, it is apparent that the synthesis of an efficient PDP phosphor goes far beyond simply achieving a particular material phase.
3.2 Phosphor Synthesis Procedure

For the synthesis of $\text{Ca}_2\text{Sr}_2\text{P}_2\text{O}_{7}:\text{Eu}$, the super reactive compounds of $\text{CaCO}_3$, $\text{SrCO}_3$, and $(\text{NH}_4)_2\text{HPO}_4$ were selected for their ability to effectively bypass the diffusion limiting issues associated with solid state reactions. The starting compounds were of ACS-REAGENT grade which averaged about 99.9% in purity. Additionally, the highest standards of laboratory technique were utilized for the prevention of secondary contamination through synthesis tools and/or equipment. Required gram quantities of the constituent powders were derived by standard stoichiometric calculations for each pyrophosphate phosphor composition of interest and measured to an accuracy of ± 0.0001 grams. The molar quantities required to produce 5 grams of the final compound were consistently used.

The host lattice component constituents were manually pulverized for ten (10) minutes by means of a mortar and pestle of medium-fine roughness and then poured into a 550ml polyethylene sample bottle containing 200ml of ethanol 95%. The relatively small quantity (1-5% mol. wt. of metal-cation) of the activator compound ($\text{Eu}_2\text{O}_3$) used, was added directly to the cloudy liquid to ensure that none was lost during the pulverization procedure. The small particle size and soft morphology of $\text{Eu}_2\text{O}_3$ allowed this to be done with no adverse effects. Approximately 75 grams of 5 mm soda lime glass beads were added to the solution for the purposes of Ball Milling, in which powders are subjected to vigorous blending and pulverization in a Sweco M18-5 vibratory grinding mill. The degree of dispersion and mixing of one reacting solid with another is important to the overall mechanism of a solid state reaction\textsuperscript{11}. Thus, it is imperative that
the pre-fired mixture is of a homogeneous nature with respect to constituent composition ratio. Additionally, the surface area of a solid varies enormously, depending on whether it is in the form of a fine powder, coarse powder, or single crystal as surface area depends on particle size. This factor has a significant influence on the solid-state reaction rate because the total area of contact between the grains of the reacting solids depends on their total surface area. However, it is important to realize that even the most rigorous grinding produces particles that are on the order of microns in size. This means that the necessary diffusion distance is similarly on the order of microns and this is a rather large distance considering the extremely slow diffusion rate of most solids. Once again, the importance of the use of reactive starting constituents to bypass the limits imposed by diffusion is apparent. Following Ball Milling, powders were separated from the Ethanol by centrifuge methods and placed in a drying oven at 82°C for twelve (12) hours before the commencement of firing procedures.

Each phosphor composition has its own unique, but required, firing cycle. Accordingly, there are certain combinations of firing time and temperature so as to obtain maximum luminescence efficiency in the so-produced phosphor. In general, there are at least four stages, which occur in the formation and development of the luminescent phase of a typical phosphor system,

1. Solid-state reaction to form the host structure.

2. Sintering to form the crystalline lattice.

3. Formation of luminescent phase and rearrangement of host crystal components.

4. Continued reaction to form a different luminescent phase, including that of a separate non-luminescent, inert phase.
The non-luminescent, inert phase is typically observed to increase with firing time and thus, it is observed that “over-firing” of a phosphor is possible.

For the pyrophosphates doped with Europium, an added step was required in order to reduce the valence state of Eu from 3+ to 2+. Blended powders were initially fired in air, and resulted in a red emitting phosphor due to the optical transitions of the Eu$^{3+}$ activator. The first firing reaction pathway for a typical Sr$_2$P$_2$O$_7$:Eu$^{2+}$ sample doped with 1% Eu (mol wt. of metal cation) is as follows:

$$1.98 \text{[SrCO}_3\text{]} + 2 \text{[(NH}_3\text{)2HPO}_4\text{]} + 0.01 \text{[Eu}_2\text{O}_3\text{]} \rightarrow$$

$$1.98\text{(SrO)}_k + 1.98\text{(CO}_2\text{)}_k + (\text{P}_2\text{O}_5)_k + 4\text{(NH}_3\text{)}_k + 3\text{(H}_2\text{O)}_k + 0.02\text{(EuO)}_k \rightarrow$$

$$\text{(Sr}_{0.98}\text{Eu}_{0.02}\text{O}_2\text{)}_k + (\text{P}_2\text{O}_5)_k = \text{Sr}_2\text{P}_2\text{O}_7:\text{Eu}^{2+} (1\% \text{ mol. wt.})$$

The Eu$^{3+}$ ion was assumed to be accompanied by a defect to promote charge neutrality in the resulting compound. The resulting powder was then vigorously pulverized using a fine mortar and pestle for five (5) minutes to break apart agglomerations and produce a fine particle morphology. Powders were then subjected to a second firing at higher temperature in a reducing atmosphere of N$_2$-H$_2$(4%) in which high crystallinity, proper phase formation, and the luminescence of Eu$^{2+}$ activators are developed. Firing procedures were performed in an Alumina tube furnace with up to eight (8) programmable cycles and a maximum temperature of 1600°C.

A further reason for the two-step firing process described above, involves the effects of particle sintering which lead to hard agglomerations during the initial solid state reaction. Sintering occurs when a system of particles is subjected to an elevated temperature and is caused by an interaction in which surfaces fuse together to form a
solid mass. It is related to a solid state reaction in that sintering is governed by diffusion processes, but no change of composition or state takes place. Actual sintering occurs by a flow of mass from each sphere to the mutual point of contact, which gradually thickens. In general, the flow rate of mass depends upon the material of interest. Any resulting agglomerations will typically lead to lower particle packing densities and a high concentration of large void spaces. As scattered light is proportional to the number and size of voids, a significant amount of light may be scattered within a phosphor displaying this morphology. Any breaking of agglomerations following the final firing procedure may serve to introduce surface defects into phosphor particles which are also known to promote the scattering of light. It was found that a fine powder of smooth surface morphology could be best achieved if these agglomerations were broken apart following the first firing as the rate of sintering action within a powder system is generally proportional to the radius of constituent particles.

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3.3 X-ray Diffraction Analysis

Structure determination was accomplished through the use of X-ray diffraction techniques. A Phillips PW1890 diffractometer equipped with a copper X-ray tube and a post sample diffractometer was utilized. A 20 step-size of 0.002 and continuous scanning angular rate of 0.008 °/sec were employed to record diffraction peaks from 20 to 80 degrees. Although all primary peaks of interest in the pyrophosphate systems produced in this work were found below 50 degrees, samples were measured to higher 20 position for the purposes of precise lattice measurement as described in the results section, 4.2.4. The x-ray spectra produced displays the intensities of the diffraction peaks as a function of the detecting angle 20. The d-spacing of these peaks may be calculated from Bragg's diffraction law, \( d = \frac{\lambda}{2 \sin \theta} \), in the first order\(^6\). The assignment of Miller indices to each reflection peak was accomplished by consultation of published data obtained from the International Center for Diffraction Data. The relative intensities of the lines of an x-ray pattern may vary assuming certain preferred orientations. Accordingly, frosted glass slides were utilized due to the need for precise measurement of phase identification throughout the composition range investigated.
3.4 Optical Spectroscopic Analysis

Photoluminescence spectroscopy is accomplished through vacuum ultraviolet (VUV) excitation followed by photon emission measurement. The entire system is presented in Figure 3.3 and can be divided into three separate steps (excitation photon production and wavelength selection, sample photoluminescence and emission control, emission wavelength selection and photon counting.

Excitation photons are produced with a Deuterium Lamp – Hamamatsu Model L1835 which is capable of efficient emission from 115 nm to 400 nm. Light produced is directed to a spherical mirror which focuses this photon stream to the entrance slit of a vacuum monochromator – ARC Model VM-502. Excitation wavelength selection is accomplished with a 1200 G/mm grating. The surface of this element is coated with Iridium which allows it to be used in the extreme ultraviolet (UV) regime. Light originating at the VM-502 entrance slit as a point source falls on the grating with the full spectrum achieved. Rotation of the grating and subsequent wavelength selection is enabled through an ARC SpectraDrive Model 748 which is computer controlled with standard LabView drivers. Photons with a specific wavelength are then focused to the entrance slit of the sample chamber. The spherical mirror housing, grating, and sample chamber are all kept under vacuum with a Turbodyne pump.

Photoluminescence activity occurs as the phosphor sample is irradiated within the sample chamber. The sample chamber is equipped with a four (4) specimen holder that utilizes 10 mm diameter by 1 mm thick cavities with MgF2 cover plates. This chamber is equipped with an output monitor as well which consists of a beam splitter and
Figure 3.1: Photoluminescence spectroscopy system layout.

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photomultiplier tube assembly. This is used to occasionally verify that the deuterium lamp output has not diminished. Photons of specific wavelength originating at the entrance slit of the sample chamber as a point source strike the flat sample surface at an angle of 60 degrees to a plane perpendicular to the central beam path. This angle (greater than 45 degrees) allows the excitation photons to interact with a greater area from which emitted photons can be measured. The path of photoluminescent emission is directed to the spectrometer as it flows from the sample chamber through a glass window. This wide beam is confined and directed to the spectrometer through the use of quartz collimating and focusing lenses. The focused light is passed through a filter which prevents any wavelength less than 335nm from entering the measurement system. Beyond this is the entrance slit of the spectrometer – ISA Model 270M.

Emission wavelength selection is accomplished with a second 1200 G/mm grating housed inside the spectrometer. Originating from the entrance slit, the photoluminescent emission fills a collimating mirror with the full spectrum where it is reflected to the grating for wavelength selection. Photoluminescent photons of specific wavelength are then passed to a focusing mirror which directs the beam to the side exit mirror enabling escape through an exit slit. All elements of the spectrometer are computer controlled using Spectromax software provided by ISA/Jobin Yvon. The entire focal length of the spectrometer is 0.27 meters. Attached to the side exit of the spectrometer is a thermoelectrically cooled photomultiplier tube (PMT) housing that contains a Hamamatsu End-On type GaAs PMT having a cutoff wavelength of 890nm. Photons originating at the spectrometer exit slit are precisely focused through this PMT by a vacuum sealed lens – PFR Spex Optics Model 20833-97. The signal from the PMT is
routed to an EG&G Princeton Applied Research 5208 Two-Phase Lock-in Amplifier, which triggers on the signal received at the same frequency and phase to that of the mechanical chopper. Only light modulated at a frequency matching that of the mechanical chopper contributes to the PL signal, as recorded by the lock-in amplifier. Depending on the material being investigated, the signal from the PMT can also be directed to a Spex DM-302 Photon Counter module. This detection method, however, must be carefully shielded from stray light, which may contribute to additional signal detection by the photon counter module. The output from either the photon counter or the lock-in is then fed into an A/D converter card residing inside a computer. To convert from wavelength to energy, the refraction index of air was taken to be ~ 1.00026, giving an energy-wavelength product of:

\[ \lambda \cdot E = 12395.2eV \cdot A^2. \]  

(3.1)
Although the sample chamber is capable of accommodating four (4) specimens, position number one (1), was always occupied by a Sodium Salicylate standard. The peak emission wavelength (under 147nm excitation) of this compound is at approximately 420nm. Therefore, this position was monitored while optics adjustments were made to ensure a consistent photon count was achieved between measured samples. Any appreciable change in the attainable value (greater than 1%) required a complete PL and PLE spectrum to be taken for use in relative quantum efficiency calculations.

PL measurement was attained by the selection of a single excitation wavelength followed by the spectroscopic scanning of multiple emission wavelengths. A scan rate of 0.5nm per step with a full one (1) second integration time was employed. The final pattern was corrected for the 1200 G/mm grating used in the spectrometer. PLE measurements involved excitation by a range of wavelengths while emitted photons were measured at a monitoring (fixed) wavelength of interest. An excitation scan rate of 12nm per minute was typically employed. The monitoring wavelength was selected as the peak position determined in PL measurement unless otherwise noted. The PMT was commanded to count photons for a specified length of time while the excitation wavelengths were scanned which produced a time versus intensity plot. In addition to (time-to-wavelength) conversion, the spectrum produced was adjusted relative to the intrinsic spectrum of the deuterium lamp which is more or less efficient at photon production depending on wavelength. For example, the Hamamatsu 1.1835 has a sharp peak in photon production of 162nm wavelength. Thus, a quantum efficiency “relative” to that of the Sodium Salicylate standard is presented.
3.5 Scanning Electron Microscopy Analysis

Particle size and surface morphology investigations were accomplished through the use of standard SEM techniques. The SEM forms an image of a sample through the application of high energy electrons which interact with the atoms of the specimen within a thin surface layer. These electron-specimen interactions involve both elastic and inelastic scattering events. The problem of charging is often observed in phosphor specimens with characteristics similar to those of insulators in which injected charges cannot readily flow to ground. The result is an accumulation of charge that causes the specimen to undergo a continually changing state of surface potential\textsuperscript{51}. A mechanism known as voltage contrast develops in which the potential distribution across the surface is imaged and can become so large that it overwhelms the contrast from true features of the specimen. A common approach utilized to overcome this effect, is to apply an extremely thin conductive carbon coating to the specimen surface. This coating is much thinner than the electron range, so that charge is still injected below the surface. The presence of the grounded, conducting coating within a micron of the injected charge provides a large voltage gradient, which leads to breakdown and subsequent discharge. However, the highly porous and clustered nature of the phosphor particles synthesized in this study led to areas in which the carbon coating could not be applied. The conducting path within virtually all particle clusters was broken and significant charging effects were observed. In response, the LEO Low-Voltage SEM was utilized for the imaging of uncoated phosphor samples. This system provides for a condition of dynamic equilibrium as the charge injected by the beam is exactly cancelled by the charge leaving the specimen\textsuperscript{51}.

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CHAPTER 4
RESULTS AND DISCUSSION

4.1 Design of Experiment

The primary goal of this research was to evaluate the ability of a europium doped pyrophosphate to effectively operate as a blue component PDP phosphor. Previous work on the Ca$_2$Sr$_3$P$_2$O$_7$:Eu phosphor system under 254nm excitation indicated that efficient blue luminescence was possible only in the α-phase due to a favorable oxygen coordination environment at Eu$^{2+}$ activator sites. These authors also found that the composition range between Ca and Sr pyrophosphate end-members provided for a complete solid-solution of the α-phase, which enabled tuning of chromaticity within the blue spectral region. As the higher energy (147nm) photons utilized in the PDP can only be absorbed through host-sensitization features, a pure phase sample space from the Ca$_2$Sr$_3$P$_2$O$_7$:Eu composition range was required for proper study of the intrinsic properties of luminescence absorption and emission.

Discovery of the most efficient blue emitting PDF phosphor from within this range required the synthesis of a potentially large number of samples due to the many production variables involved. This As discussed in section 3.2, there are several important issues to address in the synthesis process for a phosphor compound created by the solid-state reaction technique. These can generally be divided into variables associated with phosphor composition and phosphor preparation. Compositional variables include cation-cation ratio, cation-anion ratio, and cation-activator ratio, which is commonly known as activator concentration. Those variables found in phosphor

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preparation comprise blending technique and firing conditions which include ball-mill time, first firing temperature, first firing time, second firing temperature, and second firing time. It quickly becomes apparent that the total number of samples to be created would quickly become prohibitive if each variable were fully exploited to just four points as is typically desired for trend determination.

The need to investigate the pyrophosphate system in an efficient manner dictated that this potentially large number of samples be decreased through the application of variable reduction. Variables were initially fixed to allow a broad compositional survey to be performed. Upon discovery of favorable composition points with respect to luminescent performance, these initially fixed variables were expanded to produce optimum results. Thus, the reduction of variables allowed for an iterative approach to composition investigation and optimization. Variation in ball-mill time was removed with the assumption of a limiting time required for homogeneous mixing of constituent powders. The variation in activator Eu^{3+} concentration was initially removed by fixing the value at 1% molar weight of metal cation. This amount is suitable for luminescence and was minor enough as to cause no significant perturbation with respect to phase formation of the pyrophosphate host lattice. The time and temperature of the first firing step was optimized for proper completion of constituent reaction with values obtained for the most difficult case extended to all composition points of lower reactive difficulty. The second firing time was similarly arrived at and extended to all subsequent samples. The initial level of anion to cation ratio is related most directly to firing conditions and was therefore fixed at some optimum value with respect to the most difficult conditions
This method reduced the number of samples needed to produce the best blue phosphor compound considerably.

The complete synthesis and analysis plan can be viewed in the context of four (4) primary studies as described in Table 4.1. Additional investigations in support of these studies are presented within each of the results sections, 4.2 through 4.5.

Table 4.1: Experimental plan for the study of Ca₂Sr₃P₂O₇:Eu.

<table>
<thead>
<tr>
<th>Study</th>
<th>Purpose</th>
<th>Parameters Fixed</th>
<th>Parameters Varied</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Synthesis of a pure α-phase sample space of the pyrophosphate system, Ca₂Sr₃P₂O₇:Eu.</td>
<td>Eu²⁺ Concentration, Ball-Mill Time</td>
<td>Cation-Cation ratio, Cation-Anion ratio, First Firing (time/temp), Second Firing (time/temp)</td>
<td>131</td>
</tr>
<tr>
<td>2</td>
<td>Optical study of the α-phase pyrophosphate system, Ca₂Sr₃P₂O₇:Eu</td>
<td>Cation-Anion ratio, Eu²⁺ Concentration, Ball-Mill Time, First Firing (time/temp), Second Firing (time/temp)</td>
<td>Cation-Cation ratio</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>Optimization of the most favorable composition point with respect to luminescent performance.</td>
<td>Cation-Cation ratio, Ball-Mill Time, First Firing (time/temp), Second Firing (time/temp)</td>
<td>Eu²⁺ Concentration, Cation-Anion ratio</td>
<td>22</td>
</tr>
<tr>
<td>4</td>
<td>Comparison of optimized sample to BAM.</td>
<td>Cation-Cation ratio, Eu²⁺ Concentration, Ball-Mill Time, First Firing (time/temp), Second Firing (time/temp)</td>
<td>Samples are annealed at 500°C for one hour.</td>
<td>2</td>
</tr>
</tbody>
</table>
4.2 Sample Space Synthesis

4.2.1 Introduction

The efficiency of PDP phosphors is primarily influenced by host-sensitization mechanisms. Accordingly, the formation of highly crystalline host lattice structures of a pure phase character was of paramount importance to this work. The synthesis of consistently pure α-phase samples through the Ca₂₋₅Sr₂P₂O₇:Eu composition range was found to depend on the successful completion of both the first and second firing steps as discussed in the experimental procedures section. The primary purpose of the first firing step is the completion of complex precursor decomposition and initial phase formation at the particular composition of interest. This must be done while minimizing the effects of particle sintering. The second firing step allows for both the completion of final phase formation and reduction of Europium to the required divalent valence state for luminescence in the blue spectral region. Although these procedures may be studied independently due to the very different thermodynamic mechanisms involved in each, the success of the second firing step relies heavily on the first. Precursor decomposition and initial structure formation must be completed in the first firing procedure if pure phase formation is to take place in the second.

This chapter investigates the synthesis methodology required for the production of a pure α-phase sample space in the Ca₂₋₅Sr₂P₂O₇:Eu composition range. First firing conditions for metal carbonate decomposition at the most demanding end-member composition are investigated in section 4.2.2. Results indicated that the need for complete decomposition of SrCO₃ dominates the first firing step. A firing time of two
hours at 900°C was required. As the ternary join between Ca and Sr ends contain this carbonate, these conditions were extended through the composition range to achieve complete decomposition at all points. Section 4.2.3 addresses second firing conditions and compound stoichiometry required for pure α-phase production at the most difficult end-member composition. The formation of a pure α-phase in the Ca-pyrophosphate end-member was found to dominate this step and relied on both the time of firing and anion to cation (AC) ratio. It was concluded that a firing time of four hours at 1200 °C produced a pure α-phase for an anion to cation ratio less than 1.09. This limiting value was reduced to 1.05 when shorter firing times were utilized. The extension of these conditions for synthesis of the complete composition range is described in section 4.2.4 in which calculation of the degree of lattice expansion is also presented. This work indicated that expansion through the Ca₂₄Sr₂P₂O₇:Eu range displays some departure from linearity due to local deformation behavior near the Ca rich end.

4.2.2 Investigation of first firing conditions

The optimum first firing conditions required for the initial formation of phase structure rely primarily on the decomposition of the reactive metal carbonate constituent compound (MCO₃). While the phosphate source (NH₄)₃H₂PO₄, is also a reactive constituent, the lower decomposition temperature observed, ensures that any atomic scale metal oxide (MO) produced has sufficient phosphorous pentoxide (P₂O₅) to nucleate the M₃P₂O₇ structure. All the carbonates in Group II of the periodic table undergo thermal decomposition to give the metal oxide and carbon dioxide through the reaction:
\[ \text{MCO}_{3\text{d}} \rightarrow \text{MO}_{2\text{d}} + \text{CO}_{2\text{d}} \]

(4.1)

The temperature required for the decomposition of Sr based carbonates is higher than that needed for Ca based constituents. Although concentrated on the oxygen atoms, the electron charge on a carbonate is spread over the entire volume of the ion due to the similarity in the nature of C-O bonds. In this respect, the electrons are described as being delocalized\(^{41}\). When Ca\(^{2+}\) or Sr\(^{2+}\) is placed next to the carbonate ion, these delocalized electrons are pulled preferentially towards the oxygen ion closest to the positive Ca or Sr cation, resulting in a distortion that forces the remaining carbon dioxide (CO\(_2\)) to break free thus leaving the metal oxide (Figure 4.1). The thermal energy required for this action depends primarily on how polarized the carbonate molecule has become due to the presence of the metal cation. The Sr\(^{2+}\) ion has a lower charge density than Ca\(^{2+}\) because the charge is spread over a larger volume\(^{41}\). This causes less distortion to nearby negative ions and consequently, SrCO\(_3\) must be subjected to a higher temperature in order to cause the carbon dioxide to break free and leave the metal oxide. This is readily observed in the enthalpy changes for the decomposition of the various carbonates as all are strongly endothermic. The change in enthalpy for CaCO\(_3\) and SrCO\(_3\) (in kJ mol\(^{-1}\)) are +178 and +235, respectively\(^{55}\). The consequence of incomplete decomposition of SrCO\(_3\) in the first firing is the formation of the Orthophosphate compound, Sr\(_3\)(PO\(_4\))\(_2\). This may occur through the reaction of newly formed SrO with Sr\(_3\)P\(_2\)O\(_7\) in the second firing step through the reaction;

\[ \text{SrCO}_{3\text{d}} + \text{Sr}_3\text{P}_2\text{O}_{7\text{d}} \rightarrow \text{Sr}_3(\text{PO}_4)_{2\text{d}} + \text{CO}_{2\text{d}} \]

(4.2)
The delocalised electrons are pulled towards the positive ion.

This end of the ion is breaking away and becoming carbon dioxide.

Ca or Sr cation

This oxygen atom is on the way to becoming an oxide ion.

Figure 4.1: Decomposition reaction process for a metal carbonate compound.
It would seem that a simple solution to this issue would be to perform the first firing reaction at a temperature much higher than that needed for SrCO$_3$ decomposition. However, the effects of particle sintering during the first firing must be minimized in order to produce an average particle size of 10-15 microns following the second firing step. Although grinding can be performed after the second firing to reduce particle size, this procedure is expected to introduce surface defects which cause unwanted refraction effects that reduce the luminous efficiency of phosphor powders produced. Accordingly, required grinding must take place following the first firing step so that a higher temperature second firing will eliminate any surface defects. A finer particle size is typically produced if particles are not significantly sintered during the first firing procedure. Although the initial decomposition of SrCO$_3$ is primarily a function of temperature, the time at that temperature must also be considered for the complete incorporation of SrO into the lattice.

The sample space was therefore focused on variation in the first firing temperature and time. The concentration of Eu was fixed at 1% (mol wt of metal cation) to ensure that no negative effects on phase formation were encountered. The radii of Eu (1.15 Å) and Sr (1.13 Å) are within less than 15% and subsequently Vegard's law was satisfied with respect to solubility. It is typical of solid-state reactions that a small amount of one constituent will remain following completion of the reaction. This reactant is simply used up less quickly than the others. Any SrO remaining after the first firing may lead to orthophosphate production in the second. Accordingly, an excess of \((P_2O_7)^3-\) was utilized to ensure the complete incorporation of SrO into the lattice during the first firing step. The firing temperature was varied from 700 to 1000 °C and the firing
time from 1 to 4 hours. Firebricks utilized at tube ends were machined with a one inch
diameter hole to ensure that the firing environment was not static as any appreciable
partial pressure of CO₂ over the fired precursors is likely to prevent the completion of
decomposition¹¹. The complete experimental synthesis list encompasses sixteen (16)
samples as is displayed in Table 4.2. As an Alumina furnace was used for this
investigation, samples could not be readily quenched due to the required use of firebricks
at tube ends to prevent thermal shock and subsequent cracking. Accordingly, each
sample was prepared individually which necessitated rigorous control measures.
Following ball mill procedures, prefired samples were kept in tightly sealed containers
under positive nitrogen pressure until fired.

Table 4.2: Stoichiometry and first firing conditions for the synthesis of Sr₃P₂O₇:Eu.

<table>
<thead>
<tr>
<th>Sample (Label)</th>
<th>Composition (Ca:Sr) (anion/cation)</th>
<th>AC Ratio (% of cation)</th>
<th>Eu Conc. (deg°C)</th>
<th>1st Firing Conditions (hours)</th>
<th>(atmos.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>2:0</td>
<td>1.05</td>
<td>1</td>
<td>700</td>
<td>1</td>
</tr>
<tr>
<td>A2</td>
<td>2:0</td>
<td>1.05</td>
<td>1</td>
<td>700</td>
<td>2</td>
</tr>
<tr>
<td>A3</td>
<td>2:0</td>
<td>1.05</td>
<td>1</td>
<td>700</td>
<td>3</td>
</tr>
<tr>
<td>A4</td>
<td>2:0</td>
<td>1.05</td>
<td>1</td>
<td>700</td>
<td>4</td>
</tr>
<tr>
<td>A5</td>
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<td>1.05</td>
<td>1</td>
<td>800</td>
<td>1</td>
</tr>
<tr>
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<td>1</td>
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<td>2</td>
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<tr>
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<td>1</td>
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<td>3</td>
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<td>1</td>
<td>800</td>
<td>4</td>
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<td>1</td>
<td>900</td>
<td>1</td>
</tr>
<tr>
<td>A10</td>
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<td>1</td>
<td>900</td>
<td>2</td>
</tr>
<tr>
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<td>1</td>
<td>900</td>
<td>3</td>
</tr>
<tr>
<td>A12</td>
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<td>1.05</td>
<td>1</td>
<td>900</td>
<td>4</td>
</tr>
<tr>
<td>A13</td>
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<td>1</td>
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<td>1</td>
</tr>
<tr>
<td>A14</td>
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<td>1</td>
<td>1000</td>
<td>2</td>
</tr>
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<td>A15</td>
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<td>1</td>
<td>1000</td>
<td>3</td>
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<td>A16</td>
<td>2:0</td>
<td>1.05</td>
<td>1</td>
<td>1000</td>
<td>4</td>
</tr>
</tbody>
</table>

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X-ray diffraction was utilized for the structural analysis of prepared samples and relied on the qualitative comparison of the experimental spectrum to ICDD cards for SrCO$_3$ and the α-phase of Sr$_2$P$_2$O$_7$. The progression of the main peak of SrCO$_3$ was monitored as a function of first firing temperature and time. The firing temperature was found to be the main factor in decomposition with the completion of that reaction being dependent on firing time. Regardless of the firing time, all samples prepared at 700°C and 800°C displayed traces of SrCO$_3$ and it was not until 900°C that complete decomposition was observed. A small amount of metal-carbocate was observed at one hour and virtually none was found after two (Figure 4.2). A first firing procedure of 900°C for two hours was determined to be the most efficient as continued firing at a longer time or at a higher temperature lead only to additional sintering of phosphor particles.

In order to verify the necessity of this level of detail regarding the first firing procedure, the sample fired at 800°C for 2 hours and that prepared at 900°C for 2 hours were vigorously ground and subjected to a second firing in air at 1000°C for 1 hour. As displayed in Figure 4.3, the sample found to contain traces of SrCO$_3$ after the first firing, lead to a phosphor composed of primarily α-phase pyrophosphate with orthophosphate impurities following the second firing step. The presence of primary and secondary peaks of the orthophosphate form of Sr$_2$(PO$_4$)$_3$ can be clearly seen at 2θ positions near 29 and 46 degrees, respectively. In contrast, the sample indicating complete SrCO$_3$ decomposition produced only α-phase pyrophosphate.
Figure 4.2: Dependence of SrCO$_3$ decomposition in Sr$_3$P$_2$O$_7$:Eu as a function of firing temperature and time. Decomposition observed after 2 hours at 900°C.

Figure 4.3: X-ray diffraction spectra of samples A6 and A10 fired for 2 hours at 800°C and 900°C, respectively. The formation of Sr$_3$(PO$_4$)$_2$:Eu is observed in A6.
4.2.3 Investigation of second firing conditions

As described in section 2.5, the phase character of Ca₂Sr₃P₂O₈:Eu indicates a trend in which the α-phase formation temperature increases as the radius of the metal-cation decreases. Accordingly, the pure end-member Ca₃P₂O₈:Eu displays the highest temperature of final phase formation with a β to α transition at 1140°C. Accordingly, the second firing procedure is dominated by the characteristics of this end-member as both the second firing conditions (temperature and time) and ratio of anion to cation (AC) have an impact on the proper formation of the α phase. The physical mechanism of the transformation from β to α phase in the pyrophosphate, involves a shifting of the unit cell structure from tetragonal to orthorhombic through progression of the k-vector from 60° to 90°. This physical change is not instantaneous and may take place in a non-homogeneous manner throughout the sample volume. Accordingly, it was proposed that phase completion would depend strongly on firing time, as each portion of the sample volume achieved the α structure. The AC ratio was further investigated due to reported difficulties attending the preparation of homogenous samples of the pyrophosphates using the solid-state reaction technique. This was found to arise from the loss of the oxides of phosphorus by volatilization at temperatures above 1000°C\textsuperscript{62}. A portion of the phase diagram of the P₂O₅ – CaO system is presented in Figure 4.4. It was observed that the range of α phase stability is fairly narrow with respect to composition in the area of 1200°C. Therefore, the ratio of P₂O₅ to CaO remaining following the second firing was precisely controlled to ensure that a pure α-phase sample was produced.
Figure 4.4: Portion of the CaO – (P₂O₅)₆ phase diagram indicating a narrow range of α-phase stability.
The experimental sample space was focused on second firing procedure and AC ratio with Eu concentration again fixed at 1% (mol. wt. of metal-cation). The first firing procedure was fixed at 900°C for 2 hours as this was previously determined to be the most efficient means of achieving SrCO₃ decomposition and initial phase formation. Samples were fired in a Nitrogen-Hydrogen atmosphere at temperatures ranging from 1000°C to 1300°C in order to investigate the formation of both β and α phases. Firing time was varied from 2 to 5 hours and the AC ratio from 1.0 to 1.15. The complete synthesis list is presented in Table 4.3. Samples were prepared in groups of similar firing conditions with the positioning of crucibles and the black carbon utilized for Eu³⁺ reduction maintained on a consistent basis. Additionally, the flow rate of Nitrogen-Hydrogen gas was consistent for each sample group prepared.

X-ray diffraction was again the primary method utilized for structure analysis and phase identification in which experimental patterns were qualitatively compared with the ICDD cards of β and α phases of Ca₉P₂O₉. All samples prepared with an AC ratio of 1.0 were found to contain traces of the orthophosphate structure Sr₄(PO₄)₂·Eu. The relative amount remained fairly consistent and appears to be independent of either temperature or time of firing. The occurrence of orthophosphate is likely due to the volatilization of phosphorus, which yielded a ratio of Calcia (CaO) to phosphorus pentoxide (P₂O₅) of 3:1 in some areas rather than the 2:1 required for pyrophosphate production. All remaining samples fired at 1000°C and 1100°C with an AC ratio greater than 1.0 produced pure β-phase pyrophosphate. The onset of melting was observed in samples fired at 1300°C regardless of AC ratio or firing time. This is consistent with published data that places the melting temperature of Ca₉P₂O₉ at 1363°C.
Table 4.3: Stoichiometry and second firing conditions for the synthesis of Ca₃P₂O₇·Eu.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>AC Ratio</th>
<th>Eu Conc.</th>
<th>2nd Firing Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Label</td>
<td>Ca/Sr</td>
<td>anion/cation</td>
<td>% of cation</td>
<td>deg C</td>
</tr>
<tr>
<td>B1 - 4</td>
<td>2:0</td>
<td>1</td>
<td>1</td>
<td>1000</td>
</tr>
<tr>
<td>B5 - 8</td>
<td>2:0</td>
<td>1.03</td>
<td>1</td>
<td>1000</td>
</tr>
<tr>
<td>B9 - 12</td>
<td>2:0</td>
<td>1.06</td>
<td>1</td>
<td>1000</td>
</tr>
<tr>
<td>B13 - 16</td>
<td>2:0</td>
<td>1.09</td>
<td>1</td>
<td>1000</td>
</tr>
<tr>
<td>B17 - 20</td>
<td>2:0</td>
<td>1.12</td>
<td>1</td>
<td>1000</td>
</tr>
<tr>
<td>B21 - 24</td>
<td>2:0</td>
<td>1.15</td>
<td>1</td>
<td>1000</td>
</tr>
<tr>
<td>B25 - 28</td>
<td>2:0</td>
<td>1</td>
<td>1</td>
<td>1100</td>
</tr>
<tr>
<td>B29 - 32</td>
<td>2:0</td>
<td>1.03</td>
<td>1</td>
<td>1100</td>
</tr>
<tr>
<td>B33 - 36</td>
<td>2:0</td>
<td>1.06</td>
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<td>1100</td>
</tr>
<tr>
<td>B37 - 40</td>
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<td>1</td>
<td>1100</td>
</tr>
<tr>
<td>B41 - 44</td>
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<td>1100</td>
</tr>
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<td>B45 - 48</td>
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<td>1</td>
<td>1100</td>
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<td>B49 - 52</td>
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<td>1</td>
<td>1200</td>
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<td>B53 - 56</td>
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<td>1.03</td>
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<td>1200</td>
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<tr>
<td>B57 - 60</td>
<td>2:0</td>
<td>1.06</td>
<td>1</td>
<td>1200</td>
</tr>
<tr>
<td>B61 - 64</td>
<td>2:0</td>
<td>1.09</td>
<td>1</td>
<td>1200</td>
</tr>
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<td>B65 - 68</td>
<td>2:0</td>
<td>1.12</td>
<td>1</td>
<td>1200</td>
</tr>
<tr>
<td>B69 - 72</td>
<td>2:0</td>
<td>1.15</td>
<td>1</td>
<td>1200</td>
</tr>
<tr>
<td>B73 - 76</td>
<td>2:0</td>
<td>1</td>
<td>1</td>
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</tr>
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<td>B77 - 80</td>
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<td>1</td>
<td>1300</td>
</tr>
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<td>1.12</td>
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<td>1300</td>
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<td>B93 - 96</td>
<td>2:0</td>
<td>1.15</td>
<td>1</td>
<td>1300</td>
</tr>
</tbody>
</table>
Powders fired at 1200°C were found to display a much more complex variation in phase structure as a strong dependence on both AC ratio and time of firing was indicated (Figure 4.5). Samples fired for 2 hours at 1200°C produce a pure α-phase structure at an AC ratio of 1.03 and 1.06. The occurrence of β-phase was found at an AC ratio of 1.09 and only traces of the α-phase could be detected in a primarily β-phase lattice when the ratio was raised to 1.12. These results are in agreement with Figure 4.4 which displays a very narrow range of α-phase stability at 1200°C with respect to the amount of P₂O₅ present in the composition. This trend was consistently shifted with longer firing time and resulted in the ability to produce a pure α-phase sample at an AC ratio of 1.09 when fired at 1200°C for 4 hours. This is a further indication of the effects of phosphorus volatilization on α-phase formation in the pyrophosphate structure. A longer firing time required a larger amount of excess phosphorus to produce the ratio needed for α-phase formation in the narrow stability range depicted in Figure 4.4. This observation serves to highlight the significant impact that firing conditions and compound stoichiometry have on the formation of the α-phase in the pyrophosphate structure. The further influence that these parameters have on luminescent efficiency of phosphors produced will be discussed in section 4.4.3. X-ray diffraction spectra of pure β and α-phase Ca₃P₂O₇:Eu samples are presented in Figure 4.6. As can be seen, the angular position of the primary α-phase peak closely corresponds to that of a β-phase peak. This characteristic can cause difficulty in the identification of phase composition. Accordingly, care was taken to ensure that the sample surface was precisely positioned with respect to impinging x-rays within the diffractometer as any variation will lead to significant errors in peak position.
Figure 4.5: Conditions for the stability of α and β phases in Ca₃P₂O₇-Eu as a function of AC rate and second firing time. The range of α phase stability shifts with increasing firing time.

Figure 4.6: X-ray diffraction spectra of samples B35 and B59 indicating pure β and α phases, respectively.
Figures 4.7, 4.8, and 4.9 present SEM micrographs of samples fired for 4 hours at 1200°C. These images depict the progression in phase, from α to β, as the AC ratio was increased from 1.09 to 1.15. The α-phase pyrophosphate is typified by a smooth surface morphology and average particle size of approximately 15 μm (Figure 4.7). These appear to be composed of smaller particles (~4 μm) that are fused together at clearly definable boundaries. In contrast, the β-phase structure displays a relatively rough surface morphology with an average particle size of 15 μm. As in the α-phase, these particles are composed of smaller structures that are fused together at well-defined boundaries. However, these smaller particles are on the order of approximately 500 nm in the β-phase structure. As discussed in section 2.5, the transition from β to α phases involves an expansion of the unit cell as the tetragonal structure is stretched to form an orthorhombic shape. Figures 4.7 and 4.9 indicate that this transition results in a progressive fusion of (100-500 nm) particles to form much larger (3-5 μm) particles. Figure 4.8 presents a sample composed of a mixture of α and β phases. The surface morphology is characteristic of both structures with a predominantly smooth α-phase surface covered by outgrowths of the β-phase structure. Close inspection of Figure 4.7 reveals the presence of some small β-phase particles on the surface.
Figure 4.7: SEM micrograph of sample B63 at 8,000X magnification. X-ray diffraction indicated that this specimen is pure α-phase. However, some small β phase particles can be observed on the surface of the smooth α phase structure.
Figure 4.8: SEM micrograph of sample B67 at 8,000X magnification. X-ray diffraction indicated that this specimen is a mixture of α and β phases. The surface morphology well represents both structures.
Figure 4.9: SEM micrograph of sample B71 at 8,000X magnification. X-ray diffraction indicated that this specimen is pure β-phase.
4.2.4 Alpha phase synthesis through the Ca/Sr range

The results of section 4.2.2 indicated that a first firing procedure of 900°C for 2 hours was required for complete decomposition of complex precursors and proper incorporation of the resulting metal oxide into the pyrophosphate lattice in Sr₂P₂O₇:Eu. Additionally, section 4.2.3 indicated that an AC ratio of 1.06 and a 4 hour second firing procedure were required for the production of a pure α-phase pyrophosphate in Ca₃P₂O₇:Eu. These conditions were extended through CaₓSr₁₋ₓP₂O₇:Eu for the production of a pure α-phase sample space. This method does not produce a fully optimized sample at each composition point due to variation in the temperature of precursor decomposition and rate of phosphorus volatilization. However, as explained in section 4.1, the primary goal of the first study was to synthesize pure α-phase samples through the CaₓSr₁₋ₓP₂O₇:Eu composition. These samples were analyzed in the second study to determine luminescent trends with respect to spectral position of absorption and emission bands only. Any discussion of luminescent efficiency in CaₓSr₁₋ₓP₂O₇:Eu would require the full optimization of every point with respect to all variables of composition and preparation.

The Eu concentration was again fixed at 1% (mol. wt of cation) to ensure that no effects on phase formation were encountered. The complete synthesis list is presented in Table 4.4. Samples were analyzed by x-ray diffraction and qualitatively compared to ICDD cards of the pure end-member components of Ca and Sr pyrophosphate. A completely miscible α-phase was achieved with the highest degree of crystallinity found to occur approximately 100°C below the onset of melting at each composition point produced. A steady progression of primary diffraction peaks to lower 2θ positions was
observed as the molar fraction of Sr was increased in the series and is an indication of the
effects of lattice expansion (Figure 4.10). Lattice expansion occurs in a solid solution as
a larger ion is progressively substituted into the site of a smaller ion.

Table 4.4: Stoichiometry and second firing conditions for synthesis of the complete
Ca$_2$Sr$_x$P$_2$O$_7$:Eu range in the α phase.

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Composition Ca/Sr</th>
<th>AC Ratio anion/cation</th>
<th>Eu Conc. % of cation</th>
<th>2st Firing Conditions C deg</th>
<th>hours</th>
<th>atmos.</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>2:0</td>
<td>1.06</td>
<td>I</td>
<td>1200</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>D2</td>
<td>1.75:0.25</td>
<td>1.06</td>
<td>I</td>
<td>1200</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>D3</td>
<td>1.75:0.25</td>
<td>1.06</td>
<td>I</td>
<td>1100</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>D4</td>
<td>1.5:0.5</td>
<td>1.06</td>
<td>I</td>
<td>1200</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>D5</td>
<td>1.5:0.5</td>
<td>1.06</td>
<td>I</td>
<td>1100</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>D6</td>
<td>1.25:0.75</td>
<td>1.06</td>
<td>I</td>
<td>1200</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>D7</td>
<td>1.25:0.75</td>
<td>1.06</td>
<td>I</td>
<td>1100</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>D8</td>
<td>1.25:0.75</td>
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<td>I</td>
<td>1000</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
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<td>I</td>
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<td>N-H(4%)</td>
</tr>
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<td>1100</td>
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<td>N-H(4%)</td>
</tr>
<tr>
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<td>I</td>
<td>1000</td>
<td>4</td>
<td>N-H(4%)</td>
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<tr>
<td>D12</td>
<td>0.75:1.25</td>
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<td>I</td>
<td>1200</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>D13</td>
<td>0.75:1.25</td>
<td>1.06</td>
<td>I</td>
<td>1100</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>D14</td>
<td>0.75:1.25</td>
<td>1.06</td>
<td>I</td>
<td>1000</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>D15</td>
<td>0.5:1.5</td>
<td>1.06</td>
<td>I</td>
<td>1100</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>D16</td>
<td>0.5:1.5</td>
<td>1.06</td>
<td>I</td>
<td>1000</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>D17</td>
<td>0.25:1.75</td>
<td>1.06</td>
<td>I</td>
<td>1100</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>D18</td>
<td>0.25:1.75</td>
<td>1.06</td>
<td>I</td>
<td>1000</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>D19</td>
<td>0:2</td>
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<td>I</td>
<td>1000</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
</tbody>
</table>

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Figure 4.10: X-ray diffraction spectra of the Ca$_2$SrP$_2$O$_7$:Eu range. The primary peaks for Ca$_2$P$_2$O$_7$:Eu near 27° and 47° are progressively shifted to lower 2θ positions as the molar fraction of Sr is increased.
The degree of lattice expansion through the present system may be calculated based solely on the x-ray spectra produced and some basic knowledge of the pyrophosphate crystal structure. The parameter \(a\) of a cubic substance is directly proportional to the spacing \(d\) of any particular set of lattice planes. The change in 20 position of the primary peaks is also a function of this spacing \(d\). If we measure the Bragg angle \(\theta\) for this set of planes, the Bragg law, \(\lambda = 2d \sin \theta\), may be used to determine \(d\) which allows calculation of \(a\)^8. Since in general, a small change in solute concentration produces only a small change in lattice parameter, precise measurements must be made in order to determine the degree of lattice expansion as the Sr content is increased. We may reduce any error inherent in the precise position of peaks along 20 by noting that \(\lambda \sin \theta\) which appears in the Bragg relation and that this value changes very slowly with \(\theta\) near 90°. An error of 1° in \(\theta\) leads to an error of only 0.15° at \(\theta = 85°\).

Standard graphical methods are difficult to use when more than one lattice parameter is involved as is the case observed in the \(\alpha\)-phase of the \(\text{Ca}_{2},\text{Sr}_{2}\text{P}_{2}\text{O}_{7}\cdot\text{Eu}\) pyrophosphate range under investigation. The system is orthorhombic with three lattice parameters \((a, b,\) and \(c)\).

Cohen's method of lattice parameter determination is the most applicable for the present case as it provides a direct means of calculation in which \(\sin^2 \theta\) values are observed directly. The expression for an orthorhombic structure is

\[
\sin^2 \theta_{(true)} = \frac{\lambda^2}{4} \left( \frac{k^2}{a^2} + \frac{l^2}{b^2} + \frac{l^2}{c^2} \right). \tag{4.3}
\]
in which \((h,k,l)\) correspond to the miller indices, \((a,b,c)\) represent the lattice parameters, and \(\lambda\) is the wavelength of radiation utilized. This expression is then subtracted from the \(\sin^2 \theta\) (observed) value to yield the change in \(\sin^2 \theta_{\text{calc}}\). The complete expression in the case of an orthorhombic lattice is as follows:

\[
\sin^2 \theta_{\text{observed}} - \frac{\lambda^2}{4a^2} \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right) = D \sin^2 \theta.
\] (4.4)

where: \(C = \frac{\lambda^2}{4} \); \(a = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \); \(A = D/10 \); \(\delta = 10 \sin^2 \theta_0 \);

In order to solve for the individual lattice constants \((a, b, c)\), the \(C\) and \(a\) variables must be further divided into \(C_{1,2,3}\) and \(a_{1,2,3}\) as follows:

\[
C_1 = \frac{\lambda^2}{4a^2} \; ; \; C_2 = \frac{\lambda^2}{4b^2} \; ; \; C_3 = \frac{\lambda^2}{4c^2} \; ; \; a_1 = h^2 \; ; \; a_2 = k^2 \; ; \; a_3 = l^2.
\] (4.5)

The experimental values of \(\sin^2 \theta\), \(a\), and \(\delta\) are substituted into \(\sin^2 \theta = Ca + A\delta\) which is then solved for the most probable values of \(C_{1,2,3}\) and \(A\) by the method of least squares. Once \(C_{1,2,3}\) values are found, the \((a, b, c)\) lattice constants can be calculated directly from the relations given above.

Table 4.5. displays the calculated lattice parameters for each of the nine composition points in the \(\text{Ca}_{2-x}\text{Sr}_x\text{P}_2\text{O}_7: \text{Eu}\) range produced. This data is presented graphically in Figure 4.11 which indicates a progressive expansion of the lattice with
increasing Sr composition. It was observed that the lattice expansion departs slightly from linearity near the Ca-rich end. Although the radius ratio of Sr (1.13\( \cdot \)) to Ca (0.99\( \cdot \)) is less than 1.15, the Ca end-member structure must deform locally to accommodate the larger Sr cation thus producing strain effects. If this local strain increases the enthalpy of the system to sharply, a slight destabilization of the solid solution may be observed. It may be less difficult for the smaller Ca ion to substitute into a predominantly Sr-pyrophosphate lattice and thus the linear expansion of the lattice is unaffected near the Sr-rich end.

Table 4.5: Progression in lattice constants for the Ca\(_2\),Sr\(_x\)P\(_2\)O\(_7\):Eu range.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice Constants</th>
<th>Body Diagonal</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Sr</td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>0</td>
<td>8.44</td>
<td>12.52</td>
</tr>
<tr>
<td>0.125</td>
<td>8.52</td>
<td>12.64</td>
</tr>
<tr>
<td>0.25</td>
<td>8.56</td>
<td>12.72</td>
</tr>
<tr>
<td>0.375</td>
<td>8.62</td>
<td>12.82</td>
</tr>
<tr>
<td>0.5</td>
<td>8.67</td>
<td>12.91</td>
</tr>
<tr>
<td>0.625</td>
<td>8.72</td>
<td>13</td>
</tr>
<tr>
<td>0.75</td>
<td>8.76</td>
<td>13.08</td>
</tr>
<tr>
<td>0.875</td>
<td>8.82</td>
<td>13.18</td>
</tr>
<tr>
<td>1</td>
<td>8.87</td>
<td>13.27</td>
</tr>
</tbody>
</table>
Figure 4.11: Lattice expansion through the Ca$_{2-x}$Sr$_x$P$_2$O$_7$:Eu range. A small deviation from linearity is observed at the 12.5% Sr composition point.
4.3 Optical Analysis of Ca$_2$Sr$_2$P$_2$O$_7$:Eu

4.3.1 Introduction

Investigations regarding the ultraviolet excitation of calcium and strontium pyrophosphates have been reported by several authors. In each instance, the research was motivated by a desire to apply the compounds to fluorescent lighting applications and thus, all previous work has been limited to an excitation wavelength range of 200 - 300nm\textsuperscript{34}. As the PDP system utilizes photo-excitation within the vacuum ultra-violet (VUV) spectral region, the present investigation of the luminescence character of Ca/Sr pyrophosphates was performed in the 110 – 200nm range as well. Consequently, spectroscopic analysis included both host-sensitized and direct activator excitation mechanisms, which rely heavily on semiconductor band-gap theory and traditional models of photoluminescence. This task was somewhat complicated by the present lack of detailed theoretical models to describe the host lattice to activator energy migration that takes place in PDP phosphor systems\textsuperscript{43}.

This chapter presents a detailed spectroscopic investigation of phosphor samples prepared with a pure α-phase character within the Ca$_2$Sr$_2$P$_2$O$_7$:Eu composition range. Photoluminescence emission and excitation analyses of the pure Ca$_2$P$_2$O$_7$:Eu end-member are presented in section 4.3.2 in order to determine specific host-sensitization band position and efficiency. The results indicated that host-sensitization bands corresponding to both (P$_2$O$_7$)$^4^-$ and CaO bonding states are present at 124nm and 175nm, respectively. Section 4.3.3 presents a crystal field model and analysis of the expected variation in emission energy (wavelength) as the molar concentration of Sr was increased.
in the Ca₂Sr₃PO₄:Eu composition range. This procedure indicated that a linear progression to higher emission energies (lower wavelength) is to be expected as the crystal field strength is altered by the substitution of the larger Sr ion. Section 4.3.4 provides a comparison of this theoretical trend to experimental spectroscopic measurements of the pure phase composition range. The change in emission wavelength displayed a significant departure from linearity as the molar concentration of Sr was increased in the pyrophosphate lattice. Additionally, a shift to longer wavelength was observed rather than the move to shorter wavelength calculated in section 4.3.3. This behavior was explained on the basis of aperiodic perturbation models of band-gap theory and local stress effects at Eu²⁺ activator sites.

4.3.2 Optical analysis of Ca₃P₂O₇:Eu

Photoluminescence spectroscopy (PL/PLE) was utilized for the optical analysis of pure phase samples of Ca₃P₂O₇:Eu in order to uncover emission and absorption characteristics. The process is as described in the experimental procedures section, 3.5, in which 147nm VUV photons are utilized for excitation. The PL emission spectrum of pure phases indicated that the α phase is significantly more luminescent than the lower temperature β-phase (Figure 4.12). This is in agreement with the findings of Wannaker, et al and Lagos ⁷, ⁸. While the β-phase displayed only a weak emission centered at 424nm, the α phase structure produced a relatively strong emission of Gaussian shape centered at 415nm which corresponds to a blue to blue-violet color. The emission spectra of the Eu²⁺ ion consisted of a broad band due to transitions between the crystal field components of the 4f⁵5d excited state and the ⁵S₂Mos (4f⁷) ground state configuration ⁹, ¹⁰.
Figure 4.12: Photoluminescence emission spectra of Ca₂P₂O₇:Eu samples D1 and B35 representing pure α and β phases, respectively. The α phase is significantly more efficient with an intense emission band centered at 415 nm.
Photoluminescence excitation analysis of Ca₃P₂O₇:Eu was performed by monitoring the blue emission peaks while exciting the sample with a range of photons from 110nm to 300nm in wavelength. The resulting spectra shown in Figure 4.13 indicated that the entire absorption structure of the β-phase is much less pronounced than that observed in the α-phase and is likely a factor of the mixed Eu-O coordination discussed in section 2.5 of the background. The much higher measure of relative quantum efficiency of the α-phase found at the primary excitation line of 147nm is responsible for the stronger emission observed in Figure 4.13. The identification of band structure observed in the α-phase may be described in terms of absorbing complexes and proceeds from short to long wavelength (high to low energy).

As discussed in the introduction, host-sensitization features corresponding to the PO₄²⁻ complex have been observed in LaPO₄ and AlPO₄ lattices. Completed by Mishra, et al, this work involved investigation of the electronic structures of La₂O₃, AlPO₄, and LaPO₄ in order to understand the nature of optical transitions near the absorption band edge. It was observed that the density of states corresponding to the host sensitization bands from a number of phosphate phosphors, RPO₄ (R = Y, La, Gd, and Lu), were present in a narrow energy range from 7.75 to 8.61 eV which corresponds to a wavelength range of 160 to 144nm. Their calculations suggested that excitations near the absorption edge in these phosphors were associated with the phosphate groups. It was further noted that variation in the relative ordering of the phosphate antibonding states and vacant nonbonding states of the metal ions could produce variations in the band gap among rare earth phosphates. In other words, it was proposed that the structure of the host lattice directly influenced the spectral position of any phosphate host-sensitization
Figure 4.13: Photoluminescence excitation spectra of Ca₃P₂O₇:Eu samples D1 and B35 representing pure α and β phases, respectively. The α phase displays a much more pronounced absorption structure in which both direct Eu (200-300nm) and host-sensitized (110-200nm) excitation is observed.
bands present. In fact, Schwarz and co-workers observed that the spectral position of host-sensitization bands attributed to the PO$_4^{3-}$ molecule may range from 124 to 177 nm depending upon what lattice structure it is found within. These authors further stated that similar conditions were expected for diphosphates, forming oxygen-bridged PO$_4$ tetrahedra$^{65}$. This is the case observed in Ca$_3$P$_2$O$_7$:Eu where the (P$_2$O$_7$)$_2^-$ anion is formed by two PO$_4$ tetrahedra sharing an oxygen atom. Accordingly, the intense absorption band from 110 to 150 nm was attributed to the host-sensitization features of the (P$_2$O$_7$)$_2^-$ phosphate complex.

The broad absorption band from 150 to 200 nm may be attributed to host-sensitization features of the Ca-O bond and is due to a transition from the valence band to the conduction band. As discussed in section 2.3.3, excitation energy is absorbed by the host and transferred to the activator through non-resonant relaxation processes. A similar band structure was observed by Kim and co-workers in CaO:Eu where an absorption band at 205 nm was presumed to originate from host excitation of the Ca-O bonds$^{66}$. Although this band position is at longer wavelength than that observed in Ca$_3$P$_2$O$_7$:Eu, a further work by the same author on the oxyfluoride system (CaF$_2$ + CaO):Eu may explain the irregularity. This study found that the introduction of F$^-$ ions into the host lattice shifted all the absorption features to a higher energy (lower wavelength) region$^{66}$. Accordingly, it is proposed that the addition of the (P$_2$O$_7$)$_2^-$ anion is responsible for the lower wavelength (higher energy) position of the Ca-O host-sensitization band in Ca$_3$P$_2$O$_7$:Eu.
The direct absorption of excitation energy by Eu-O bonds is observed from 200 to 300nm. The relative quantum efficiency of 1.80 observed at 254nm excitation is in agreement with previous work on this compound for use in lamp technology. Wannaker attributed absorption peaks at 240 and 340nm observed in Ca₂P₂O₇:Eu to the direct absorption of UV photons by the Eu²⁺ activator. Although the PLE spectra of figure 4.3.2 extends to 300nm only, the start of the longer wavelength absorption band found by Wannaker can be clearly seen from 290 to 300nm. The separation of Eu²⁺ (4f-5d) transitions into two bands in a strontium-metaphosphate Sr(PO₄)₂ host lattice was reported by Ebendorff and Ehrt. They observed that the 8-fold coordinated sites of cubic symmetry found in Sr(PO₄)₂:Eu²⁺, resulted in a splitting to eₙ orbitals at lower energy and t₂₉ orbitals at higher energy. As the Eu²⁺ activator is similarly coordinated in the α-phase Ca₂P₂O₇ host lattice, the two bands observed in Figure 4.13 are attributed to a splitting of 5d orbitals into t₂₉ orbitals from 200 to 290nm and eₙ orbitals starting at 290nm.

4.3.3 Theoretical variation in crystal field strength

As a consequence of the reduction of Eu to the 2⁺ state, the f-d transition is highly sensitive to the octahedral field due to the removed shielding of f-electrons by the d-orbital. Accordingly, the progressive change in lattice constant observed throughout the Ca₂SrP₂O₇:Eu range was expected to effect a change in the crystal field strength parameter 10Dq. As discussed in section 2.6, the 10Dq parameter describes the separation distance between doubly degenerate eₙ and triply degenerate t₂₉ orbitals of the
5d configuration of Eu$^{2+}$. This parameter has a dependence on bond length, ion charge, and ion radius as follows:

$$Dq = \frac{Ze^3}{6a^3} \{e^4\}. \quad (4.6)$$

where $Z$ is the charge or valence of the ion, $e$ is the charge of the electron, and $a$ is the bond length. The change depends on three parameters. Two of them, $Z$ and $e$, characterize the charge on the ligand oxygen ion $O^{2-}$, which has a value of $Z^{267}$. The bond length between $O^{2-}$ and Eu$^{2+}$ is taken to be half the body diagonal of section 4.2.4.

In an effort to determine the theoretical variation in emission energy expected by the progressive substitution of Sr ions through the Ca$_2$Sr$_x$P$_2$O$_7$:Eu range, the lattice constants for each composition point calculated in section 4.2.4 were applied to the above crystal field strength relation. In the present case, we may utilize the body diagonal, $(a^2+b^2+c^2)^{1/2}$, of the lattice as the proportion of $a$, $b$, and $c$ are observed to remain fairly constant throughout the composition range. Table 4.6 lists the results of these calculations and Figure 4.14 displays the information graphically. The $10Dq$ parameter increases from 0.148eV to 0.166eV as the molar fraction of Sr is increased. This progressive increase in transition energy indicates that Sr$_2$P$_2$O$_7$:Eu is expected to produce a lower wavelength photon emission than Ca$_2$P$_2$O$_7$:Eu.

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Table 4.6: Results of the theoretical calculation of 10Dq in a phase Ca₃SrₓP₂O₇:Eu.

<table>
<thead>
<tr>
<th>Composition</th>
<th>bond length (Å)</th>
<th>ion charge (eV)</th>
<th>ion radius (Å)</th>
<th>10Dq (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.99</td>
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<td>1.15</td>
<td>0.148</td>
</tr>
<tr>
<td>0.125</td>
<td>8.06</td>
<td>2</td>
<td>1.15</td>
<td>0.150</td>
</tr>
<tr>
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<td>8.12</td>
<td>2</td>
<td>1.15</td>
<td>0.153</td>
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<td>8.17</td>
<td>2</td>
<td>1.15</td>
<td>0.155</td>
</tr>
<tr>
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<td>0.157</td>
</tr>
<tr>
<td>0.625</td>
<td>8.27</td>
<td>2</td>
<td>1.15</td>
<td>0.160</td>
</tr>
<tr>
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<td>8.32</td>
<td>2</td>
<td>1.15</td>
<td>0.162</td>
</tr>
<tr>
<td>0.875</td>
<td>8.37</td>
<td>2</td>
<td>1.15</td>
<td>0.164</td>
</tr>
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<td>1</td>
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<td>1.15</td>
<td>0.166</td>
</tr>
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Figure 4.14: Theoretical variation in crystal field strength $10D_q$ through the $\alpha$ phase of $Ca_2Sr_3P_2O_7:Eu$. An increasing $10D_q$ parameter indicates that an emission shift to higher energy (lower wavelength) should occur as the Sr composition is increased.
4.3.4 Optical analysis of Ca$_{0.5}$Sr$_{0.5}$O$_2$:Eu

Photoluminescence analysis of the Ca$_{0.5}$Sr$_{0.5}$O$_2$:Eu composition range resulted in an emission trend that was significantly different from the theoretical model calculated in the previous section. A steady progression in peak position of a parabolic nature with a maximum wavelength of 441 nm at the 50:50 molar ratio was observed (Figure 4.15). A similar effect was reported by Cardona with respect to alloys of the silver and cuprous halides$^{68}$. He found that several of the exciton peaks fitted a relation of the form,

$$\Delta E = Cx (1-x). \quad (4.7)$$

where, $\Delta E$ is the departure from linearity in eV, $C$ is a constant, and $x$ is the molar concentration of one alloy in the system. This was described as an aperiodic (second-order) perturbation of the crystal potential at a metal site arising from disorder in the system. This disorder will be a maximum when $x = 0.5$ or when there are equal number of A and B atoms in an AB system. Thompson and Woolley expanded this relation to the general case of a solid-solution of any two binary compounds and found that the energy bandgap has a quadratic dependence on composition $x$ as follows:

$$E(x) = a + bx + cx^2. \quad (4.8)$$

where the nonlinear bowing parameter $c$ is four times the deviation of $E$ from linearity at the equimolar concentration ($x = 0.5$). The other two parameters ($a$ and $b$) are determined by the values of $E$ observed for the pure compounds$^{69}$. 

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Figure 4.15: Photoluminescence emission spectra of $\alpha$ phase $\text{Ca}_{2-\lambda}\text{Sr}_\lambda\text{P}_2\text{O}_7: \text{Eu}$. The emission progression is parabolic instead of linear and the Sr end-member emits with a lower rather than higher energy.
Much like Cardona, Thompson and Woolley invoked the effects of microscopic inhomogeneity in the crystal potential with substitutional alloying, which goes as \( x(1-x) \), to justify the quadratic variation of their formula. In the absence of any theoretical information on the expected variation of the parameter \( C \), they developed an empirical relation between \( C \) and the mean energy gap \( E_{\text{on}} \) for the component compounds of the alloy system of the form,

\[
C = 0.3 \ E_{\text{on}}^{-1/2}. \tag{4.9}
\]

The bowing parameter, \( C \), measures the effect on the direct gap between conduction and valence bands of perturbation due to the aperiodic component of the crystal potential\(^69\). Since the interaction between such bands increases as \( E_{\text{on}} \) decreases, a relation of such a form is not unreasonable. Application of this theory to the observed emission spectra of the \( \text{Ca}_2\text{Sr}_2\text{P}_2\text{O}_7\cdot\text{Eu} \) range is as follows (415nm = 2.9876eV & 420nm = 2.9521eV):

\[
E_g(Ca - \text{pyro}) = 2.9876eV \ & \ E_g(Sr - \text{pyro}) = 2.9521eV. \tag{4.10}
\]

\[
E_{\text{on}} = \frac{2 \cdot 2.9876eV + 2.9521eV}{2} = 2.96985eV = 417nm. \tag{4.11}
\]

\[
C = 0.3E_{\text{on}}^{-5/2} = 0.3(2.96985^{-5/2}) = 0.17408eV. \tag{4.12}
\]

\[
E_{\text{on}} - C = 2.96985eV - 0.17408eV = 2.79577eV = 443nm. \tag{4.13}
\]
This theoretical calculation is in excellent agreement with experimental data obtained and indicates that the departure from linearity observed in the Ca$_2$Sr$_2$P$_2$O$_7$:Eu range is caused by an aperiodic perturbation of the crystal potential. However, the position of Ca and Sr end-member emissions are the inverse from that predicted by the crystal field strength model of section 4.3.3 as well. Based on virtual crystal field analysis, the emission of the Ca end-member is expected to be at a longer wavelength than that of the pure Sr compound. Radiative emissions from Eu$^{2+}$ ions are due to f-d transitions and the energy splitting of the d-state by the native crystal field 10Dq decreases monotonically from Ca$_2$P$_2$O$_7$:Eu to Sr$_2$P$_2$O$_7$:Eu. Since radiation occurs corresponding to an electron transition from the lower d-level to the ground state, a smaller value of 10Dq generally gives a shorter peak wavelength. It was proposed that this irregularity is caused by stress fields that can occur in substitutional alloy systems in which there is a mismatch between the ionic radii of the cations. Kasano found that local stress imposed on activator ions from the neighboring lattice (denoted as type I stress) is an important factor in peak shifts as found in the above results$^{50}$. According to the configurational coordinate model, the distance R between the lowest energy points of two adiabatic potential curves, which represent the excited state and the ground state, is governed by electron-phonon coupling. We may assume that the Sr$_2$P$_2$O$_7$:Eu end-member effectively experiences no stress fields as the ionic radius of Sr (1.13 Å) is very close to that of Eu$^{2+}$ (1.15 Å). However, in the case of Ca$_2$P$_2$O$_7$:Eu, R shrinks because the lattice constant of Ca$_2$P$_2$O$_7$ differentially expands around the Eu$^{2+}$ ion incorporated into the smaller Ca (0.99 Å) lattice site. If this is so, a shift of the excitation spectrum to longer wavelength must be simultaneously observed as bond lengths increase$^{50}$. Indeed,
PLE spectra of these samples indicates a shift to longer excitation wavelength. This can best be observed by following the transition point between the optical edge of the ($P_{2}O_{7}$)$^{4-}$ and CaO host-sensitization bands as shown in Figure 4.16. This position increases monotonically from 150nm to 155nm as the molar fraction of Sr is increased in the pyrophosphate lattice. Consequently, it was determined that type I stress fields are responsible for the anomalous spectral position of the $Ca_{2}P_{2}O_{7}$:Eu emission observed.
Figure 4.16: Photoluminescence excitation spectra of a phase Ca$_2$Sr$_2$P$_2$O$_7$:Eu. A shift in the optical edge of the phosphate absorption band to longer wavelength is observed as the Sr composition is increased.
4.4 Optimization of CaSrP₂O₇:Eu for Luminescence Efficiency

4.4.1 Introduction

Production of the α-phase solid solution as described in section 4.2.4, was accomplished through the variation of only two of the eight synthesis parameters discussed in section 4.1. This reduction in variables was achieved by thorough optimization procedures at the end-member compositions of CaP₂O₇:Eu and SrP₂O₇:Eu. Although additional optimization was possible at each of the nine composition points produced, the determination of general luminescent trends with respect to spectral position of absorption and emission bands was achieved. With an emission wavelength of 441 nm, the equimolar composition of CaSrP₂O₇:Eu was found to provide the most favorable chromaticity character in the previous section, 4.3.4. It was observed that the emission intensity of the Ca₂ₓSr₁₋ₓP₂O₇:Eu range improved as the molar fraction of Sr was increased in the pyrophosphate lattice and is in agreement with the study by Lagos in which a similar composition range was produced with fixed synthesis variables. It was proposed that this trend is principally a function of the increased solubility of Eu²⁺ within the lattice as the Sr²⁺ ion was progressively added due to its larger size and lower measure of charge density. Additionally, the decrease in second firing temperature utilized as the composition progressed to the Sr-rich end was expected to have an effect on the final AC ratio due to decreasing phosphorus volatilization. Accordingly, it was expected that variation in the previously fixed variables of Eu concentration and AC ratio would yield an improvement in the absorption efficiency and subsequent emission intensity of CaSrP₂O₇:Eu.

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This chapter presents an investigation into the effects of optimization on the luminescence efficiency and emission intensity of CaSrP₂O₇:Eu. Optimization of the Eu²⁺ concentration is presented in section 4.4.2 where a value of 2% was found to provide for the most intense photon emission. A variation in this value with respect to excitation wavelength was observed and is discussed. Investigation regarding the most optimum AC ratio is described in section 4.4.3 in which a ratio of 1.02 (anion to cation) produced the highest measure of host absorption efficiency and emission intensity. Section 4.4.4 focuses on the effect of flux addition where an improvement in Eu solubility was observed and corresponds to an increase in efficiency across the entire excitation spectral range.

4.4.2 Optimization of Eu²⁺ concentration

The Eu²⁺ concentration had been fixed at 1% (mol. wt. of metal-cation) to this point as only the general trends in luminescence performance through the composition range of interest were sought. As discussed in the previous section, it was expected that the optimum amount of Eu²⁺ found may change as a function of Sr composition. There is always an optimum activator concentration required to produce the greatest measure of luminescent efficiency in a phosphor system and is in general, a function of the plurality of localized phonon modes present in the host lattice¹⁴. The emission intensity, Iₑm, is directly proportional to the number of activator centers present, Nₐ, and is inversely proportional (an exponential function) to the number of quenching centers, Nq. These quenching centers may be nearest neighbor activator sites, which dissipate energy by direct exchange or distant sites accessible by resonant exchange mechanisms. It is

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observed that when the activator concentration becomes too high, a loss in luminescence efficiency is observed. Initially, the emission intensity is linearly proportional to the number of emitting activator sites, Na. At some point, the density of these sites becomes too large and the overall emission intensity falls, at an exponential rate, as concentration increases. This can best be understood through the theory of virtual photon exchange in which a photon emitted by one excited luminescent center may be captured by another center, which subsequently becomes excited. If there is an assembly of radiators, the excitation energy from a single emitted photon can be passed from site to site until it reaches a non-radiative energy sink where it is dissipated as phonon energy\textsuperscript{11}.

The sample space studied encompasses a range of Eu concentration from 0.5 to 5\% (mol. wt. of cation). An AC ratio of 1.06 was utilized with the first and second firing conditions of 900°C/2hrs and 1100°C/4hrs, respectively. The complete synthesis list is presented in Table 4.7.

Table 4.7: Stoichiometry and firing conditions utilized for the optimization of Eu\textsuperscript{2+} concentration in a phase CaSrP\textsubscript{2}O\textsubscript{4}:Eu.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>AC Ratio</th>
<th>Eu Conc.</th>
<th>2st Firing Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Label</td>
<td>Ca/Sr</td>
<td>anion/cation</td>
<td>% of cation</td>
<td>deg C</td>
</tr>
<tr>
<td>E1</td>
<td>1:1</td>
<td>1.06</td>
<td>0.5</td>
<td>1100</td>
</tr>
<tr>
<td>E2</td>
<td>1:1</td>
<td>1.06</td>
<td>1</td>
<td>1100</td>
</tr>
<tr>
<td>E3</td>
<td>1:1</td>
<td>1.06</td>
<td>1.5</td>
<td>1100</td>
</tr>
<tr>
<td>E4</td>
<td>1:1</td>
<td>1.06</td>
<td>2</td>
<td>1100</td>
</tr>
<tr>
<td>E5</td>
<td>1:1</td>
<td>1.06</td>
<td>2.5</td>
<td>1100</td>
</tr>
<tr>
<td>E6</td>
<td>1:1</td>
<td>1.06</td>
<td>3</td>
<td>1100</td>
</tr>
<tr>
<td>E7</td>
<td>1:1</td>
<td>1.06</td>
<td>3.5</td>
<td>1100</td>
</tr>
<tr>
<td>E8</td>
<td>1:1</td>
<td>1.06</td>
<td>4</td>
<td>1100</td>
</tr>
<tr>
<td>E9</td>
<td>1:1</td>
<td>1.06</td>
<td>4.5</td>
<td>1100</td>
</tr>
<tr>
<td>E10</td>
<td>1:1</td>
<td>1.06</td>
<td>5</td>
<td>1100</td>
</tr>
</tbody>
</table>
X-ray diffraction indicated no identifiable change in phase or crystallinity with increasing Eu$^{2+}$ content. This may be an effect of the favorable cation radius ratio found which allows Eu$^{2+}$ (1.15 Å) to readily enter the lattice thus allowing the compound to follow Vegard's law within this relatively small substitutional concentration range. Photoluminescence analysis at 147 nm excitation presented an efficiency to concentration relationship that corresponds well to the classical model of luminescence quenching behavior in phosphor systems. The optimum level of Eu concentration was observed at 2% (mol. wt. of cation) as is displayed in Figure 4.17 and provides a 50% improvement in emission intensity with respect to samples prepared in the previous study, section 4.2.4. The PLE spectra of this sample space, displayed a difference in the concentration dependence of host sensitization and direct activator excitation on Eu$^{2+}$ composition that warrants further discussion (Figure 4.18). Higher Eu$^{2+}$ concentration results in a larger defect concentration due to the small difference in Eu$^{2+}$ (1.15 Å) relative to the Ca$^{2+}$ (0.99 Å) or Sr$^{2+}$ (1.13 Å) ion that it substitutes for. When excited directly by 200 nm to 300 nm photons, all the Eu$^{3+}$ centers are simultaneously raised to the excited state. As the crystal field splitting of 5d orbitals in Eu$^{2+}$ is primarily a function of nearest neighbor ions, the effects of defect formation on luminescence efficiency is expected to be significant. In contrast, the application of 110 nm to 200 nm photons results in the excitation of only those activators properly positioned with respect to host absorbing complexes. Subsequently, the effects of defect formation will affect a smaller number of Eu$^{2+}$ emitting centers and thus allow for a higher activator concentration to be used.
Figure 4.17: Dependence of PL emission intensity on \( \text{Eu}^{2+} \) concentration in a phase \( \text{CaSrP}_2\text{O}_6: \text{Eu} \). A value of 2% (molar wt. of metal cation) is found to provide the most intense emission.
Figure 4.18: Photoluminescence excitation spectra of a phase CaSrP₂O₄:Eu samples E2 and E4 representing Eu concentrations of 1% and 2%, respectively. Improvement in (P₂O₅)²⁻ and (Ca,Sr)O host-sensitization bands are observed at 125nm and 175nm, respectively. Direct Eu absorption does not follow the same concentration dependence.
The optimum activator concentration with respect to the peak of \((\text{P}_2\text{O}_5)^+\) absorption states is as found in PL spectra under 147\(\text{nm}\) excitation. A value of 2\% produces the most intense photon emission resulting in the highest value of relative quantum efficiency at 147\(\text{nm}\) excitation (Figure 4.18). However, the spectral region of direct activator excitation displays no change in relative quantum efficiency at an activator concentration of 2\%. Photoluminescence analysis of samples studied under 254\(\text{nm}\) excitation indicated that a Eu\(^{2+}\) concentration greater than 1.5\% was found to display the effects of luminescence quenching. This lower optimum activator concentration may be due to the higher degree of defect sensitivity that directly excited Eu\(^{2+}\) activators display.

4.4.3 Optimization of AC ratio

It was determined in section 4.2.3, that an anion-cation ratio of 1.06 produced a pure \(\alpha\)-phase while providing a sufficient measure of crystallinity for luminescent trend investigation in the \(\text{Ca}_{2-x}\text{Sr}_x\text{P}_2\text{O}_7\):Eu range. It was proposed that a lower firing temperature utilized for the formation of \(\text{CaSrP}_2\text{O}_7\):Eu may allow for a smaller AC ratio due to less volatilization of phosphorus ions. In formulating a phosphor composition, one often employs a small excess of the anionic reactant so as to avoid the presence of strongly absorbing cationic species in the end product\(^{11}\). In the case of \(\text{CaSrP}_2\text{O}_7\):Eu under photo-excitation in excess of 200\(\text{nm}\), the anion complex is typically inert and thus results in no loss of luminescent efficiency. However, application of the high energy (short wavelength) VUV photons utilized in the PDP results in absorption by both cation (CaO, SrO) and anion (P\(_2\)O\(_5\))\(^+\) complexes. Accordingly, a more precise level of this
stoichiometric ratio was expected to enhance the efficiency of both cation and anion complex host sensitization bands in CaSrP$_2$O$_7$:Eu, thus leading to an improved emission intensity.

The experimental sample space was focused on the variation in anion-cation (AC) ratio within the CaSrP$_2$O$_7$:Eu composition. The Eu$^{2+}$ concentration was fixed at 2% (mol. wt of cation) as determined in the previous procedure with first and second firing conditions again fixed at (900°C/2 hrs) and (1100°C/4 hrs), respectively. A range of AC ratios from 1.0 to 1.06 were prepared in steps of 0.005 leading to a total of thirteen (13) sample compositions. The complete synthesis list is presented in Table 4.8. All samples were prepared simultaneously to ensure that firing conditions were identical for each composition.

Table 4.8: Stoichiometry and firing conditions utilized for the optimization of the AC ratio in a phase CaSrP$_2$O$_7$:Eu.

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Composition</th>
<th>AC Ratio anion/cation</th>
<th>Eu Conc. % of cation</th>
<th>1st Firing Conditions deg C</th>
<th>hours</th>
<th>atmos.</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>1:1</td>
<td>1</td>
<td>2</td>
<td>1100</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>F2</td>
<td>1:1</td>
<td>1.005</td>
<td>2</td>
<td>1100</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>F3</td>
<td>1:1</td>
<td>1.01</td>
<td>2</td>
<td>1100</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>F4</td>
<td>1:1</td>
<td>1.015</td>
<td>2</td>
<td>1100</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>F5</td>
<td>1:1</td>
<td>1.02</td>
<td>2</td>
<td>1100</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>F6</td>
<td>1:1</td>
<td>1.025</td>
<td>2</td>
<td>1100</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>F7</td>
<td>1:1</td>
<td>1.03</td>
<td>2</td>
<td>1100</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>F8</td>
<td>1:1</td>
<td>1.035</td>
<td>2</td>
<td>1100</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>F9</td>
<td>1:1</td>
<td>1.04</td>
<td>2</td>
<td>1100</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
<tr>
<td>F10</td>
<td>1:1</td>
<td>1.05</td>
<td>2</td>
<td>1100</td>
<td>4</td>
<td>N-H(4%)</td>
</tr>
</tbody>
</table>

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X-ray diffraction analysis was utilized to elucidate any changes in crystallinity as a function of AC ratio. However, any variation observed could not be consistently repeated when multiple samples were analyzed from within the same phosphor lot produced. This is an indication that the effects of preferred orientation encountered during sample preparation far outweighed any improvement in crystallinity over the small range of AC ratio investigated. The only consistently measurable effect was the occurrence of orthophosphate impurities at the stoichiometric ratio of 1.0 and is in agreement with results found in section 4.2.3 on the pure Ca pyrophosphate end-member.

Photoluminescence analysis displayed a reliance of both host-sensitization and direct activator band structure on the AC ratio. The PLE spectra presented in Figure 4.19, indicates an improvement in both cation and anion complex absorption bands as the AC ratio was decreased from 1.06 to 1.02. This is likely due to the lower occurrence of unincorporated anion complexes as any excess P_2O_7 present may absorb ultraviolet photons without transferring excitation energy to Eu^{2+} activators. This bound energy will dissipate through phonon emission only as these disjoined anion complexes have no vibronic coupling to the pyrophosphate lattice. Support for this argument was found in the observation of improvements in metal-oxide and direct Eu absorption bands from 150 to 300 nm. Although unincorporated P_2O_7 anion complexes do not absorb 254 nm photons, their presence is expected to perturb the long-range order of the lattice thus, decreasing luminescence efficiency. A further reduction in the AC ratio resulted in a loss of absorption efficiency brought on by the occurrence of orthophosphate phase regions. PL results indicated that an AC ratio of 1.02 is optimum (Figure 4.20). This lead to a 10% improvement in emission intensity with respect to the samples of section 4.4.2.
Figure 4.19: Photoluminescence excitation spectra of α phase CaSrP₂O₇:Eu samples E4 and F5 representing AC ratios of 1.06 and 1.02, respectively. Improvement in both host-sensitization and direct activator excitation bands are observed.
Figure 4.20: Dependence of PL emission intensity on AC ratio in a phase CaSrP$_2$O$_7$·Eu.

A value of 1.02 is found to provide the most intense emission. A value below 1.015 is accompanied by the occurrence of the orthophosphate structure which significantly decreases emission intensity.
4.4.4 Effects of NH₄Cl flux addition

It was proposed that the use of a flux material in the second firing procedure may serve to enhance activator ion incorporation within the host lattice structure. A flux is defined as an additive, that does not effect the reactants during the firing cycle, yet promotes crystal growth of the final product. It does so by providing a liquid phase for transport of material, including ions, so as to increase the crystallinity of the particles so-produced [1]. A 1% (mol. wt. of metal cation) amount of NH₄Cl was blended into a CaSrP₂O₇:Eu sample prior to the second firing step. The stoichiometry and firing conditions for this compound were as determined most optimum in the previous study, section 4.4.3.

Photoluminescence analysis indicated improvement in activator ion incorporation. This can most readily be seen through PLE spectra of samples with and without flux addition. The utilization of NH₄Cl resulted in an increase in relative quantum efficiency throughout both host-sensitization and direct activator excitation regions (Figure 4.21). As discussed in section 2.4, the ability of Eu³⁺ activators to efficiently emit photons at 441nm in the CaSrP₂O₇:Eu structure is directly effected by the crystal field that they experience. This crystal field is primarily a function of the oxygen coordination environment at Eu³⁺ sites. Accordingly, an increase in the number and quality of octahedrally coordinated Eu²⁺ ions is expected to increase the 441nm emission. As the emission is monitored to produce the PLE spectra of Figure 4.21, the entire spectral range (110nm to 300nm) will display an improved efficiency. This improved efficiency resulted in a further increase in emission intensity of 2% relative to the sample prepared in the previous study on AC optimization.
Figure 4.21: Photoluminescence excitation spectra of α phase CaSrP₂O₇:Eu samples F5 and F5f which includes NH₄Cl flux (1% mol wt. of metal cation) prior to the second firing step. Improvement in host-sensitization and direct activator excitation bands are observed and is attributed to increased Eu²⁺ solubility within the lattice.
4.4.5 Summary of optimization results

The optimization procedures utilized in this third study resulted in an 80% improvement in emission intensity with respect to the samples analyzed in section 4.2.4 (Figure 4.22a). This increase is a direct function of improvements in host-sensitization band structure at 147nm primary and 172nm secondary excitation lines. Observation of the entire PLE spectra of the optimized CaSrP2O7:Eu sample indicates a significant measure of improvement in (P2O7)6- and metal-oxide absorption band structure resulting in 214% and 173% increases, respectively (Figure 4.22b). The region of direct activator excitation was improved as well with approximately 100% gains in efficiency observed.

It is important to note that the lowest point in the quantum efficiency curve (150nm) corresponding to the edge of phosphate absorption states has changed very little. As discussed in section 4.3.2, the spectral position of the 125nm host-sensitization band in CaSrP2O7:Eu is a function of the density of states of the phosphate complex. Accordingly, its position was not expected to vary unless a change in phosphate bonding character occurred.
Figure 4.22: PL (a) and PLE (b) spectra of CaSrP$_2$O$_7$:Eu displaying improvement due to optimization procedures.
4.5 Comparison of CaSrP$_2$O$_7$:Eu to BAM

4.5.1 Introduction

The original intent of this research was to determine the ability of a europium doped pyrophosphate to effectively function as a blue component PDP phosphor. Accordingly, the optimized CaSrP$_2$O$_7$:Eu sample discussed in section 4.4.4 were quantitatively compared to the current blue component phosphor, BAM. Of the several measures of phosphor performance discussed in the background section, three are of particular importance to this work (chromaticity, efficiency, and stability). Chromaticity involves the spectral position and saturation characteristics of any photon emission produced. Efficiency refers to the degree that a phosphor can effectively absorb and convert excitation energy to produce this photon emission. Finally, stability, in the case of a PDP phosphor, describes the measure of luminescence efficiency retained following the harsh manufacturing conditions encountered.

This chapter presents the quantitative comparison of CaSrP$_2$O$_7$:Eu to BAM with respect to chromaticity, efficiency, and stability. The structure and spectral characteristics of luminescence emission are discussed in section 4.5.2 in which samples are quantitatively compared in terms of the resulting CIE chromaticity coordinates produced. It was determined that CaSrP$_2$O$_7$:Eu compares favorably to BAM as the chromaticity coordinates of $x=0.16$ and $y=0.05$ resulted in a deeper blue emission. Section 5.4.3 presents a comparison of the efficiency of CaSrP$_2$O$_7$:Eu to that displayed by BAM where it was found that the absorption bands attributed to (P$_2$O$_7$)$^{6-}$ (125nm) and EuO (200-300nm) states are significantly more efficient than those of BAM. However, the spectral position of the sharp phosphate absorption edge observed in CaSrP$_2$O$_7$:Eu
with respect to the primary PDP excitation line at 147\text{nm} resulted in an emission intensity only 30\% that of BAM. The luminescence efficiency of \(\text{Ca}_2\text{Sr}_2\text{P}_2\text{O}_7\cdot\text{Eu}\) and BAM following a burn-in simulation are discussed in section 5.4.4. Favorable stability performance was observed as \(\text{Ca}_2\text{Sr}_2\text{P}_2\text{O}_7\cdot\text{Eu}\) retained 94\% of luminescence efficiency, whereas BAM maintained approximately 65\% under the same conditions.

4.5.2 Comparison of Emission Characteristics

A primary requirement for a blue component PDP phosphor is that it displays a photon emission of Gaussian character centered at 450nm, which corresponds to a saturated blue color. As discussed in the background section, the eye acts as an integrating instrument and will quickly sense a reduction in color saturation or purity if this Gaussian spectrum is too broad. Accordingly, the shape and half width of an emission is a facet that heavily influences the quality of a blue component PDP phosphor. Figure 4.23 presents a comparison of the normalized photoluminescence emission spectra of \(\text{CaSrP}_2\text{O}_7\cdot\text{Eu}\) and BAM. The peak in photon emission of \(\text{CaSrP}_2\text{O}_7\cdot\text{Eu}\) was found at 441nm and that of BAM at 458nm. Thus each was slightly displaced from the optimum spectral position of 450nm deemed most desirable for blue luminescence. A more significant difference is found when comparing the shape of these spectra with respect to FWHM and the degree of color purity. The FWHM value of \(\text{CaSrP}_2\text{O}_7\cdot\text{Eu}\) and BAM emissions were approximately 40nm and 50nm, respectively. In particular, BAM displayed some overlap into the green spectral region found at 520nm which causes the eye to interpret the emission as a lighter hue of blue and lower degree of saturation than the deep blue observed in \(\text{CaSrP}_2\text{O}_7\cdot\text{Eu}\).
Figure 4.23: Normalized PL emission spectra of CaSrP$_2$O$_7$:Eu (sample F5) and as-received BAM. The CaSrP$_2$O$_7$:Eu phosphor displays a smaller FWHM value and does not extend into the green spectral region at 520nm. This results in an improved color purity versus BAM.
The spectra in Figure 4.23 was utilized for the purpose of quantitative analysis through the application of trichromatic theory as discussed in the background section (2.6.2) in which tristimulus values (X, Y, and Z) may be calculated for each spectrum of interest. Chromaticity coordinates (x and y) were then determined through normalization functions of the tristimulus values. A Fortran 90 program, CIE4, was utilized for this procedure and provided CIE values of (x = 0.16 , y = 0.046) for CaSrP$_2$O$_7$:Eu and (x = 0.15 , y = 0.086) for BAM (Table 4.9). Figure 4.24 displays the position of these coordinates within the CIE chromaticity diagram. Note that each point is very close to the ideal blue position observed in the CRT blue component with x = 0.15 and y = 0.06. Although the x-value of BAM better matches this position, the y-value of CaSrP$_2$O$_7$:Eu was found to be superior to both BAM and the CRT blue component. The larger y-coordinate of BAM was a direct result of the overlap into the green spectral region that its emission band displays in Figure 4.23.

Table 4.9: Calculation of CIE coordinates for optimized α phase CaSrP$_2$O$_7$:Eu, BAM, and the blue component phosphor used in the P22 set.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Emission Peak</th>
<th>CIE coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>nm</td>
<td>x</td>
</tr>
<tr>
<td>F5</td>
<td>450</td>
<td>0.16</td>
</tr>
<tr>
<td>BAM</td>
<td>458</td>
<td>0.15</td>
</tr>
<tr>
<td>CRT Blue</td>
<td>441</td>
<td>0.15</td>
</tr>
</tbody>
</table>

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Figure 4.24: CIE chromaticity diagram displaying both CaSrP$_2$O$_7$:Eu (sample F5) and BAM. Although slightly positioned at a greater x-coordinate, the y-coordinate of CaSrP$_2$O$_7$:Eu is improved with respect to both BAM and the CRT blue standard phosphor.
4.5.3 Comparison of Luminescence Efficiency

The brightness of a luminescent emission is the attribute we use to describe the perceived intensity of light. In the case of a blue component PDP phosphor, brightness is a direct function of the efficiency associated with the conversion of VUV photo-excitation to photon emission in the blue spectral region. Accordingly, luminescence efficiency at the primary (147nm) and secondary (172nm) excitation lines of the Xe plasma utilized in the PDP was the principal measure of comparison in this work. Photoluminescence (PLE and PL) spectra of CaSrP$_2$O$_7$:Eu and BAM are presented in Figure 4.25. It was observed that the host-sensitization band attributed to (P$_2$O$_7$)$_3$$^{2-}$ states centered at 125nm is significantly more efficient than the host lattice absorption states of BAM (Figure 4.25a). Similarly, the region of direct Eu$^{2+}$ activator excitation states from 200nm to 300nm favors the pyrophosphate as well. However, the presence of a sharp absorption edge associated with the phosphate group (125nm to 150nm) caused a loss of quantum efficiency relative to the primary excitation line of 147nm and resulted in an emission intensity of only 30% that of BAM (Figure 4.25b). Although the spectral position of this absorption band was seen to shift slightly to longer wavelength with Sr addition in figure 4.16 of section 4.3.4, the degree of change is not sufficient to effectively alter the situation. As approximately 82% of photo-excitation energy arrives with this 147nm wavelength, the current CaSrP$_2$O$_7$:Eu phosphor was not deemed suitable as an effective blue component PDP phosphor. On the other hand, the high quantum efficiency of the phosphate absorption band indicates that phosphate phosphors have the potential to effectively function in the PDP if the phosphate absorption band can be better positioned.
Figure 4.25: PLE (a) and PL (b) spectra of CaSrP₂O₇:Eu (sample F5) and BAM.

Although higher in efficiency, the (P₂O₇)³⁻ host-sensitization band is poorly positioned with respect to the 147 nm primary excitation line of the PDP.
4.5.4 Comparison of Stability Character

As discussed in the introductory chapter, the blue PDP phosphor BaMgAl\(_{10}\)O\(_{17}:\text{Eu}^{2+}\) (BAM) suffers losses in luminescence efficiency of 30% or more following a burn-in process required for panel manufacture. This deterioration of blue component luminescence is one of the most significant shortcomings in current PDP technology\(^1\). It was the favorable performance of some phosphate lamp phosphors under a similar manufacturing step that prompted the study of the current pyrophosphate system. Accordingly, the optimized CaSrP\(_2\)O\(_7:\text{Eu}\) sample and a specimen of BAM were subjected to a 500°C anneal firing for one hour in an air atmosphere to simulate the burn-in conditions encountered in actual panel manufacture. Samples were fired in flat-bottomed alumina crucibles placed immediately adjacent to one another.

The effect on the luminescence efficiency character of BAM was similar to that reported in previous work and resulted in a loss of 37% emission intensity (Figure 4.26a). The primary factor that led to this luminescent degradation was an alteration in the host-sensitization band structure from 120nm to 170nm which directly corresponds to the region of VUV excitation (Figure 4.26b). Additionally, the band structure in the 200nm to 300nm region corresponding to direct Eu excitation has uniformly degraded which would tend to support earlier work, which indicated that Eu oxidation is not the reason for losses in efficiency associated with BAM. The band structure from 260nm to 300nm continued to display the beginning of a second band which corresponds to the lower energy \(\text{I}_{\text{2}}\) state of \(\text{Eu}^{2+}\). The absorption of excitation energy by the \(\text{Eu}^{2+}\) ion is typified by a single broad charge transfer (CT) band.
Figure 4.26: PL (a) and PLE (b) spectra of as-received and annealed BAM. The 37% reduction in PL emission intensity observed is due to a degradation of host-sensitization efficiency at 147nm and 172nm.
A significant measure of improvement in stability was observed in the CaSrP₂O₇:Eu sample subjected to the same annealing conditions. A loss in emission intensity of only 6% was found following thermal treatment, which corresponds well with previous work on phosphates used in lamp applications (Figure 4.27a). Investigation of the host-sensitization structure indicated that both (P₂O₇)⁴⁻ and (Ca, Sr)O bonding states remained unaltered which is in stark contrast to the effect noted in BAM (Figure 4.27b). Additionally, the retention of quantum efficiency in the region of direct Eu²⁺ activation was improved as well. The beginning of the t₁₂ state of Eu³⁺ can again be seen very near 300nm in the annealed sample. Comparison of this sample to the annealed BAM specimen indicates that the difference in intensity has decreased significantly. The heat-treated CaSrP₂O₇:Eu displayed an emission intensity 50% that of a similarly treated BAM sample (Figure 4.28a). This was primarily due to a decrease in the luminescence efficiency difference between CaSrP₂O₇:Eu and BAM along the 147nm excitation line as seen in Figure 4.28b.
Figure 4.27: PL (a) and PLE (b) spectra of CaSrP$_2$O$_7$:Eu (sample F5) and the sample specimen following a 500°C anneal. The observed loss of only 6% PL emission intensity is due to the retention of host-sensitization structure.
Figure 4.28: PL (a) and PLE (b) spectra of (sample F5-annealed) and annealed BAM. The PL emission intensity of CaSrP$_2$O$_7$:Eu versus BAM is improved due to the superior stability of its host-sensitization structure.
CHAPTER 5
CONCLUSIONS

The objective of this research was to investigate the photoluminescence properties of Ca$_{2-x}$Sr$_x$P$_2$O$_7$:Eu$^{3+}$ in order to determine its effectiveness as a blue component PDP phosphor. This involved the completion of four (4) primary studies: (i) synthesis of a pure α-phase sample space within the Ca$_{2-x}$Sr$_x$P$_2$O$_7$:Eu$^{3+}$ range, (ii) spectroscopic study of this range to determine the character of host-sensitization features and emission trends, (iii) optimization of the composition displaying the best chromaticity with respect to luminescence efficiency, and (iv) comparison of this optimized sample to the phosphor currently used in PDP systems, BAM. This work was accomplished through the use of X-ray diffraction, photoluminescence emission spectroscopy (PL), photoluminescence excitation spectroscopy (PLE), and SEM analysis techniques.

As the PDP phosphor relies primarily on host-sensitization for transfer of VUV excitation energy to activator sites, highly crystalline host lattices of a pure phase character were required for the study of intrinsic properties of luminescence efficiency. The synthesis of a pure α-phase pyrophosphate sample space was accomplished by extending the conditions required for pure phase production at end-members through the Ca$_{2-x}$Sr$_x$P$_2$O$_7$:Eu$^{3+}$ range. The need for complete decomposition of SrCO$_3$ was found to dominate the Sr$_2$P$_2$O$_7$:Eu end-member composition and required a first firing procedure of 900°C for two (2) hours. Occurrence of the orthophosphate, Sr$_2$(PO$_4$)$_3$, structure was observed when samples containing residual SrCO$_3$ were subjected to a second firing procedure due to the reaction of newly formed SrO and Sr$_2$P$_2$O$_7$:Eu. The higher α-phase
formation temperature observed in the Ca$_2$P$_2$O$_7$:Eu end-member composition was found to control the procedures utilized in the second firing step. Synthesis of a pure α-phase relied heavily on both AC ratio and second firing time. It was determined that volatilization of the oxides of phosphorus at temperatures above 1000°C lead to a boundary of allowed AC ratio that tightly controlled α-phase stability. Samples fired at 1200°C for two (2) hours displayed an α-phase boundary of 1.03<AC<1.06 in which values below or above these limits lead to the occurrence of orthophosphate or β-phase, respectively. The upper limit of this boundary was observed to increase with a longer second firing time due to the increase in phosphorus volatilization. The conditions determined optimum for the synthesis of a pure α-phase in Ca$_2$P$_2$O$_7$:Eu were extended through the Ca$_{2-x}$Sr$_x$P$_2$O$_7$:Eu$^{2+}$ range resulting in a solid-solution of the α-phase. This was verified by the progressive shift of primary x-ray diffraction peaks to lower 2θ position as the molar fraction of Sr was increased in the pyrophosphate lattice. Cohen's method of lattice constant determination was utilized throughout the α-phase Ca$_{2-x}$Sr$_x$P$_2$O$_7$:Eu$^{2+}$ range to quantitatively calculate the degree of lattice expansion. A linear progression was observed with the exception of a slight destabilization of the lattice found at the Ca:Sr (1.75:0.25) composition point. It was proposed that this occurred as a result of differential expansion of the Ca-rich lattice due to initial substitution of the larger Sr ion. It was theorized that this local strain may have decreased as the composition progressed to the Sr-rich end due to the greater ease of substituting the smaller Ca (0.99 Å) ion into Sr (1.13 Å) lattice sites.

In order to understand the character of host-sensitization features and emission trends within the Ca$_{2-x}$Sr$_x$P$_2$O$_7$:Eu$^{2+}$ range, photoluminescence (PL/PLE) analysis was
performed. Determination of absorption band structure focused on the Ca$_2$P$_2$O$_7$:Eu end-
member as this point represented the highest measure of optimization with respect to AC
ratio thus far. Recall that the value determined most optimum at this composition point
was simply extended to remaining points through the Ca$_2$Sr$_x$P$_2$O$_7$:Eu$^{2+}$ range. 
Photoluminescence emission analysis indicated that the α-phase was significantly more
luminescent that the lower temperature β-phase structure, which is in agreement with
previous studies on this phosphor under 254nm excitation. The α-phase produced a
broad emission band of Gaussian shape with a peak position of 415nm. This emission
was attributed to transitions between the crystal field components of the 4f$^{6}$5d excited
state and the $^5$S$_{5/2}$ (4f$^5$) ground state configuration of the Eu$^{2+}$ activator ion in octahedral
coordination. Photoluminescence excitation analysis of this emission displayed well-
defined host and Eu$^{2+}$ absorption structures. The band from 110 to 150nm was attributed
to host-sensitization features of the phosphate (P$_2$O$_7$)$^{6-}$ group and is in agreement with the
density of states calculations of Mishra and experimental observations by Schwarz which
yield a range of 125 to 175nm for the absorption band edge of the PO$_4$$^{3-}$ complex. The
broad band structure from 150 to 200nm was assigned to host absorption by the (Ca,Sr)-O
bonds which is in close agreement to observations made by Kim and co-workers on
CaO:Eu. The absorption band extending from 200nm to longer wavelengths was
determined to arise from the direct excitation of the Eu$^{2+}$ activator ion. The splitting of
t$_{2g}$ and e$_g$ orbitals into high and low energy bands by the crystal field was identified by
the observation of a prominent dip located at 290nm.

Calculation of the theoretical variation in crystal field strength, 10Dq, was
performed in order to predict the shift in emission energy (wavelength) as the
composition progressed through the Ca$_2$-Sr$_2$P$_2$O$_7$:Eu$^{2+}$ range. The value of 10Dq was found to vary from 0.148eV at Ca$_2$P$_2$O$_7$:Eu$^{2+}$ to 0.166eV at Sr$_2$P$_2$O$_7$:Eu$^{2+}$. These results predicted that the emission of Eu$^{2+}$ in the pyrophosphate lattice would progress to higher transition energies (lower wavelength) as the molar fraction of Sr was increased. Spectroscopic (PL) analysis of the Ca$_2$-Sr$_2$P$_2$O$_7$:Eu$^{2+}$ range displayed an emission trend that departed significantly from the linear profile predicted by these crystal field strength calculations. A parabolic emission trend was observed with a maximum wavelength of 441nm found at the equimolar composition point of CaSrP$_2$O$_7$:Eu$^{2+}$. Furthermore, a longer wavelength emission of 420nm was observed at the Sr$_2$P$_2$O$_7$:Eu$^{2+}$ end-member rather than the shorter wavelength emission predicted through 10Dq calculations. The occurrence of a parabolic emission profile in the Ca$_2$-Sr$_2$P$_2$O$_7$:Eu$^{2+}$ range was examined using semiconductor band-gap theory. It was determined that this profile arose from an aperiodic perturbation of the crystal potential due to disorder arising from the mixing of dissimilar Ca and Sr ions which follows a composition model of x(1-x). The x variable corresponds to the molar fraction of either Ca or Sr in the lattice. Theoretical calculations of the expected variation in band-gap energy between Ca and Sr-based end-members lead to a predicted emission wavelength of 443nm, which closely matched the 441nm experimental result. The occurrence of a longer wavelength emission from Sr$_2$P$_2$O$_7$:Eu relative to the Ca-based phosphor was proposed to originate from Type I stress fields which may occur due to the difference in the radius of substitutional ions in a solid-solution. It was determined that the 420nm emission of Sr$_2$P$_2$O$_7$:Eu was as expected due to a close match in the radius of Sr$^{2+}$ (1.13 Å) relative to Eu$^{2+}$ (1.15 Å). Accordingly, the 10Dq calculations indicated that the emission of Ca$_2$P$_2$O$_7$:Eu should have been at a longer
wavelength rather than the shorter 415nm emission observed. It was proposed that this anomaly arose from the influence of Type I stress fields caused by the difference in radius of Ca (0.99 Å) and Eu²⁺ (1.15 Å) ions.

Although CaSrP₂O₇:Eu²⁺ was found to provide the best emission with respect to chromaticity or emission wavelength, the luminescence efficiency was not optimized as the conditions required for pure α-phase production in the Ca-based end-member were simply extended through the Ca₂Sr₂P₂O₇:Eu²⁺ range. Accordingly, the Eu²⁺ concentration and AC ratio were optimized for luminescence efficiency. A Eu²⁺ concentration of 2% (mol. wt. of metal cation) was found to provide the highest emission intensity with respect to 147nm photo-excitation as the onset of luminescence quenching was observed when the concentration was raised above this optimum value. Photoluminescence excitation analysis revealed that the activator concentration dependence of direct Eu²⁺ absorption at 254nm excitation did not follow the same profile as that observed along the 147nm excitation line associated with host-sensitization features. When excited directly by 254nm photons, the optimum Eu²⁺ concentration was found at 1.5% rather than 2%. It was proposed that the observed difference in concentration dependence arose from a higher sensitivity to defect formation in the case of direct Eu²⁺ excitation. An optimized AC ratio of 1.02 was found to provide a further improvement in emission intensity. It was proposed that the lower ratio directly benefitted host-sensitization structure due to the strong absorption character of unincorporated P₂O₅. Direct activator bands were expected to benefit from the general increase in long-range order within the pyrophosphate lattice. Finally, the effect of flux addition prior to second firing procedures was investigated. An increase in the
luminescence efficiency of the entire spectral region was observed and is attributed to an improved degree of Eu\(^{3+}\) solubility in the crystalline lattice. The optimization procedures utilized resulted in an 80% improvement in the emission intensity of CaSrP\(_2\)O\(_5\):Eu\(^{3+}\). The efficiency of host-sensitization bands corresponding to (P\(_2\)O\(_5\))\(^+\) and (Ca,Sr)-O were improved by 214% and 173%, respectively. An increase of 100% was achieved in the direct Eu\(^{3+}\) excitation band as well.

In order to determine the effectiveness of CaSrP\(_2\)O\(_5\):Eu\(^{3+}\) as a blue component PDP phosphor, a comparison of its spectral properties to those of BAM was made with respect to chromaticity, luminescence efficiency, and thermal stability. Although the emission peak of both CaSrP\(_2\)O\(_5\):Eu\(^{3+}\) and BAM were slightly displaced from the ideal wavelength of 450 nm observed in the CRT blue component phosphor, the smaller FWHM (~40 nm) of the CaSrP\(_2\)O\(_5\):Eu\(^{3+}\) emission was found to yield an improved color purity. The larger FWHM (~50 nm) of BAM resulted in overlap of the emission spectra into the green region at 520 nm and resulted in a CIE coordinate y-value of 0.086, which is 40% higher than the y = 0.06 provided by the CRT blue component phosphor. The CaSrP\(_2\)O\(_5\):Eu\(^{3+}\) emission displayed a y-value of 0.046 which is an improvement over both BAM and the CRT blue component phosphor. Photoluminescence excitation spectra indicated that the phosphate host-sensitization band in CaSrP\(_2\)O\(_5\):Eu\(^{3+}\) displayed a relative quantum efficiency that is greater than BAM by a factor of two. However, the spectral position of the sharp optical edge of this band relative to the 147 nm primary excitation line of the PDP resulted in an emission intensity only 30% that of BAM.

Although the position of the band edge was observed to shift slightly to longer wavelength with increasing Sr content, the degree of this change was not sufficient to
alter the situation considerably. This performance was somewhat improved following a 500°C anneal of CaSrP₂O₇:Eu²⁺ and BAM used to compare the thermal stability of both phosphors. While the annealed BAM specimen suffered a 37% degradation in emission intensity, a similarly treated CaSrP₂O₇:Eu²⁺ sample was observed to lose only 6% of its original luminescence output. Photoluminescence excitation spectra of annealed samples indicated that while BAM displayed a breakdown in host-sensitization structure, CaSrP₂O₇:Eu²⁺ fully retained the structure of (P₄O₇)⁶⁺ and (Ca,Sr)-O absorption bands.

These results indicate that although highly efficient host-sensitization is possible in a pyrophosphate host lattice doped with divalent europium, the phosphate absorption edge is not favorably positioned with respect to the 147nm primary excitation line utilized in the PDP system. However, the large relative quantum efficiency displayed by this band and the excellent thermal stability found in CaSrP₂O₇:Eu²⁺ strongly suggests that further work on variations of the phosphate group is warranted.
CHAPTER 6
FUTURE WORK

Continued work is focused on the discovery of phosphate phosphors that have host-sensitization bands properly positioned for 147nm photo-excitation. These host lattice structures must also provide an octahedral coordination environment for Eu\textsuperscript{2+} activator ions and remain stable during burn-in simulation procedures. As discussed in section 4.3.4, the spectral position of host-sensitization features is not significantly altered by cation substitution within a phosphate host lattice. Rather, their spectral position is primarily a function of P-O bonding character. This subject was addressed for Eu\textsuperscript{2+} doped fluoride phosphate and meta-phosphate glasses by Eberhoff and Ehrl\textsuperscript{33}. The fluoride phosphate system is characterized by PO\textsubscript{4} groups bonded into the chains of fluoroaluminates. In contrast, the meta-phosphate glass contains individual PO\textsubscript{4} groups, which form long polyphosphate chains. This results in a higher fraction of non-bridging oxygen ions observed in the meta-phosphate lattice. It was noted that the fluoride phosphate host-sensitization bands occurred at a lower wavelength (higher energy) than those of the meta-phosphate structure. Eberhoff and Ehrl proposed that the longer wavelength position of the host absorption band observed in the meta-phosphate structure was due to the higher fraction of non-bridging oxygen ions present. NMR and Raman spectroscopy indicated that although the electron donor power of fluoride phosphate was higher than that found in meta-phosphate, the oxygen polarizability was lower. They attributed this to the presence of fluoride ions having lower polarizability than oxide ions, which resulted in a lower degree of the entire covalency of all bonds of rare-earth ions in
the fluoride phosphate system as compared with the meta-phosphate structure. The higher covalency between rare-earth ions and ligands in the meta-phosphate system resulted in a lower value of inter-electronic repulsion. Accordingly, the 4f-5d transition energy of Eu$^{3+}$ would be expected to occur at a lower energy (longer emission wavelength). This theory may help to explain the phosphate absorption band positions observed in Ca$_2$Sr$_2$P$_2$O$_7$:Eu$^{3+}$ and La$_{1-x}$Gd$_x$PO$_4$ at 124-125nm and 149-150nm, respectively. The former pyrophosphate lattice is typified by bridging oxygen ions whereas, none are observed in the latter orthophosphate system.

In an effort to determine the effect of individual PO$_4$ tetrahedra on host-sensitization of a Eu$^{3+}$ doped phosphate phosphor, Sr$_4$(PO$_4$)$_2$:Eu$^{3+}$ was synthesized in the α phase which provides an octahedral coordination environment. Photoluminescence spectroscopy revealed that the host-sensitization band corresponding to PO$_4$ groups occurred at 145nm. A Eu$^{3+}$ emission centered at 430nm was observed and corresponded to a 100% improvement over the 441nm emission of CaSrP$_2$O$_7$:Eu$^{3+}$. However, the intensity of this emission was decreased by 35% following burn-in simulation procedures due to a loss of host-sensitization structure similar to that observed in BAM.

It was proposed that bridged PO$_4$ group structure, may be responsible for the higher stability observed in CaSrP$_2$O$_7$:Eu$^{3+}$. Accordingly, it is proposed to use 1+ cations in an orthophosphate lattice to create a similar bridged phosphate structure that provides an absorption environment typified by individual PO$_4$ tetrahedra. The proposed structure is of the form M$^+$M$^+$PO$_4$:Eu$^{3+}$ where M = Ca, Sr, Ba and M$^+$ = Na, K. The Na and K ions allow PO$_4$ tetrahedra to bridge without significantly effecting the electron donor power of bonded oxygen ions. Orthophosphates of this form were studied by M.S. Waite under
254nm photo-excitation for application to the fluorescent lighting industry\textsuperscript{71}. The resulting Eu\textsuperscript{2+} emissions from 430 nm to 455 nm were observed to depend directly on the type of metal cations utilized in the host lattice. Pure phase samples representing the six variations possible with the above cations (Ca, Sr, Ba, Na, K) must be prepared and analyzed for host-sensitization and emission structure in the VUV region. This will determine if the structure benefits from the individual PO\textsubscript{4} tetrahedra character. The stability of these phosphors following burn-in simulation is to follow. This will evaluate the degree to which 1\textsuperscript{+} cations can effectively create a stable network structure.
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