Solid State Lighting Program

FINAL REPORT

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Phosphors for near UV-Emitting LEDs for Efficacious Generation of White Light

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1. EXECUTIVE SUMMARY

- 1) We studied phosphors for near-UV (nUV) LED application as an alternative to blue LEDs currently being used in SSL systems. We have shown that nUV light sources could be very efficient at high current and will have significantly less binning at both the chip and phosphor levels. We identified phosphor blends that could yield 4100K lamps with a CRI of approximately 80 and $LPW_{nUV,opt}$ equal to 179 for the best performing phosphor blend. Considering the fact that the lamps were not optimized for light coupling, the results are quite impressive. The main bottleneck is an optimum blue phosphor with a peak near 440 nm with a full width half maximum of about 25 nm and a quantum efficiency of >95%. Unfortunately, that may be a very difficult task when we want to excite a phosphor at ~400 nm with a very small margin for Stokes shift. Another way is to have all the phosphors in the blend having the excitation peak at 400 nm or slightly shorter wavelength. This could lead to a white light source with no body color and optimum efficacy due to no self-absorption effects by phosphors in the blend. This is even harder than finding an ideal blue phosphor, but not necessarily impossible.
- 2) With the phosphor blends identified, light sources using nUV LEDs at high current could be designed with comparable efficacy to those using blue LEDs. It will allow us to design light sources with multiple wattages using the same chips and phosphor blends simply by varying the input current. In the case of blue LEDs, this is not currently possible because varying the current will lower the efficacy at high current and alter the color point. With improvement of phosphor blends, control over CRI could improve. Less binning at the chip level and also at the phosphor blend level could reduce the cost of SSL light sources.
- 3) This study provided a deeper understanding of phosphor characteristics needed for LEDs in general and nUV LEDs in particular. Two students received Ph.D. degrees and three undergraduates participated in this work. Two of the undergraduate students are now in graduate school. The results were widely disseminated – 20 archival journal publications (published, accepted or in preparation) and three conference proceedings resulted. The students presented their work at 11 different national/international conferences (32 oral or poster presentations) and the PI's delivered 12 invited, keynote or plenary lectures.

2. PROJECT DESCRIPTION

2.1 OBJECTIVES – OVERVIEW OF RESEARCH PLAN

Task list:

1. Identification and development of novel phosphors for near UV LED source excitation ($\lambda_{\text{ex}} = 370 - 410 \text{ nm}$)
 - a. Search for novel host lattice-sensitizer-activator combinations for efficient absorption and emission
 - b. Nano-size phosphors for reduced scattering
 - i. Optimized for strong absorption in near UV and negligible visible absorption and low scattering coefficient in both visible and UV range
 - c. Targeted quantum efficiency $\sim 95\%$
2. Development of core/shell nanophosphors
3. Electrophoretic deposition of phosphors
 - a. Conformal distribution
 - b. “Remote phosphor” configuration
 - i. Extraction efficiency (η_{ext}) ultimately $\sim 95\%$
4. Identification of phosphor blends for optimal CRI and CCT
5. Fabricate LED white-emitting lamp
 - a. Efficacy near 140 LPW

2.2 IDENTIFICATION OF HOST/ACTIVATOR COMBINATIONS

Identification of host/activator combinations will be performed by theoretical and analytical calculations, mainly based on the method developed by Dorenbos¹. In this method, the emission wavelength of a wide band gap phosphor composition is a function of the energy of the free ion activator (E_F), the crystal field depression, $D(A)$ and the Stokes shift, $S(A)$. The main question is then to identify hosts in which the $4f$ -to- $5d$ excitation energy will lie in the spectral range of 380-400 nm. During the last few years, Dorenbos empirically studied this problem and observed that energy, $E_a(RE^{3+}, A)$ (RE = rare earth element) required to excite a $4f$ electron to the lowest $5d$ level split by the crystalline field depends on the free ion energy, $E_F(RE^{3+})$ and crystal field depression in host, A given by $D(A)$ is:

$$E_a(RE^{3+}) = E_F(RE^{3+}) - D(A) \quad (1)$$

This interesting relationship shows that excitation energies depend on two parameters: one depending on the rare earth ion and other depending on the host lattice A . This equation provides a theoretical framework to explore $4f$ -to- $5d$ transitions for a rare earth ion in a given host, if the $5d$ -to- $4f$ transition energy is available for one rare earth ion in that host. The emission energies, $E_e(RE^{3+}, A)$ also satisfy a similar relationship:

$$E_e(RE^{3+}) = E_F(RE^{3+}) - D(A) - S(A). \quad (2)$$

$S(A)$ describes the Stokes shift in host A and is independent of the rare earth ions. Similar relations have been found to be valid for divalent ions. The validity of these expressions has been established both empirically and by a priori calculations for rare earth ions in solids.

Both Eqs.1 and 2 have been found to be valid within $\pm 500 \text{ cm}^{-1}$. Values of $E_F(RE^{3+})$ are available for most ions. An extensive list of $D(A)$ has been tabulated by Dorenbos for trivalent

¹ P. Dorenbos, "The 5d level positions of the trivalent lanthanides in inorganic compounds," J. Lumin. 91, 155 (2000).

rare earth ions and a somewhat smaller list for divalent ions. For Ce^{3+} , $E_a(Ce^{3+}, A)$ can be shown to be:

$$E_a(Ce^{3+}) = 49340(cm^{-1}) - D(A). \quad (3)$$

Thus, for excitation in the spectral range of 380-400 nm, hosts with $D(A)$ ranging from 23025-24340 cm^{-1} are needed. These are rather high values of $D(A)$ and can be obtained in iodides, some oxides, oxy-halides, sulfides and oxy-nitrides. A quick inspection of the data reported by Dorenbos reveals about twenty-four host lattices, some of which are employed as hosts for phosphors for UV LEDs. For some of them, $S(A)$ is also available which can be used to predict the $5d$ -to- $4f$ emission energies. A thorough search of literature together with some exploratory studies of Ce^{3+} ions in yet to be considered novel hosts based on crystal structure data (for example the Inorganic Crystal Structure Database, ICSD) could add potential candidates for Ce^{3+} activation.

2.3 NANOCRYSTALLINE PHOSPHORS

Nanophosphors can be fabricated by a variety of chemical synthesis methods: combustion, co-precipitation and sol gel processing. In a combustion reaction, metal nitrates and a fuel (carbohydrazide or urea) are combined and the reaction is initiated at low temperature. The reaction is highly exothermic, resulting in a flame with a temperature in excess of 1200°C. The resulting powders are nanocrystalline and single phase. In co-precipitation, a basic solution is added to an acidic aqueous solution of atomically mixed elements, resulting in precipitation of hydrous oxides that are subsequently heated at low temperatures to drive off residual organics and water. The nanocrystalline powders typically need to be heated to high temperatures to fully crystallize the structure.

Core-shell formation at the nanoscale is broadly used to stabilize nanoparticles or nanowires to enhance their optical, catalytic and magnetic properties. It has been shown that coating with both organic and inorganic shells, particularly inorganic shells, significantly enhances the photoluminescence of nanoparticles, due to the effective passivation of surface states that cause the non-radiative recombination of electron and holes in semiconductor nanocrystals.

2.4 ELECTROPHORETIC DEPOSITION OF PHOSPHORS

Electrophoretic deposition (EPD) is a technique in which charged particles dispersed in a liquid are deposited onto a substrate under the force of an applied electric field. EPD has many advantages besides its benign processing conditions, such as a high uniformity, the possibility of producing deposits fast and continuously, and a low level of contamination. The EPD cell simply consists of two vertical, parallel electrodes held in polycarbonate plates separated by a fixed distance. The cathode typically is a removable conducting substrate on which a LED diode can be connected surrounded by a stainless steel ring to create a uniform electric field. The anode is platinum gauze. The apparatus is placed in a beaker containing the slurry and connected to a high voltage, potentiostatic power supply.

2.5 IDENTIFICATION OF PHOSPHOR BLENDS

Using the spectral power distribution (SPD) of red, green and blue phosphors selected on the basis of fluorescence measurement, phosphor blends will be formed to achieve the desired color coordinates and color temperatures compatible with high efficacy. Our main objective will be to develop a white light source at 4100K CCT with CRI > 80. Such blend modeling programs are routinely used within OS for phosphor application in fluorescent lamps.

2.6 FABRICATION OF UV-LED LIGHT SOURCE

Device fabrication will primarily take place using the phosphor layers developed at UCSD, and UV-emitting LED sources from within the company or obtained from commercial vendors. Using internally developed UV-LEDs at OSRAM Opto-Semiconductors will facilitate earlier integration of the technology developed in this project to a product. Several configurations are possible. Chips may be mounted either in a chip-on-board manner onto a flat substrate or mounted into a commercial LED package. Phosphor will be applied either in a “remote phosphor” configuration being developed at OS or applied directly on the chip as mentioned earlier.

2.7 COMPARISON TO EXISTING TECHNOLOGY

Fig. 1 compares the existing white-emitting light source in (a) with the proposed design in (b). Several significant differences are notable. First is the use of a UV-emitting LED instead of a blue-emitting LED. Second, nanophosphors with a core/shell morphology are deposited in a ‘remote phosphor’ configuration, on top of a transparent substrate. Third, the color coordinates, CRI and CCT can be finely tuned through use of various phosphor blends.

Using red-, green- and blue-emitting phosphors it will be possible to improve the CRI and CCT over that of the YAG:Ce³⁺/blue-emitting LED. The extraction efficacy will be improved through utilization of nanophosphors configured with a remote phosphor design. The near-UV LED has less binning, which result in less lamp-to-lamp variation and a smaller current droop. All of these contribute to an improved white-emitting light source. Additionally, there is accessibility to any color through color conversion.

Fig. 1. Comparison of (a) current blue-emitting LED coupled with a yellow-emitting phosphor (YAG:Ce³⁺) and (b) proposed design with a UV-emitting LED with a blend of phosphors.

3. PROJECT ACTIVITIES

The research results from Tasks 1-6 are discussed in this section.

1. Phase I
 - a. Task 1: Identification of phosphors for excitation in the spectral range of 370-410 nm (OS)
 - b. Task 2: Synthesis and optimization of candidate phosphors for quantum efficiency greater than 95% (OS, UCSD)
2. Phase II
 - a. Task 3: Development of core/shell nanophosphors (UCSD)
 - b. Task 4: Successful development for integrating the phosphor with the LED by electrophoretic deposition (UCSD)
3. Phase III
 - a. Task 5: Development of phosphor blends for white light generation (OS)
 - b. Task 6: Fabrication of simple white light sources using candidate phosphor blends and LEDs with efficacy near 165 lpw_{opt} (OS)

Note: This project was given a 6-mo. no-cost extension due to the delay in OS starting the project. The final agreement between UCSD and OS was not signed until 06/10, approximately nine months after UCSD started the project. However, we have caught up with our task progress. The project was also given a 6-mo. no-cost extension, from 03/28/13 to 09/30/13.

3.1. PROJECT PARTNERS AND ROLES

This is a collaborative work between UC San Diego (La Jolla, CA) and Osram Sylvania (Central Research, Beverly MA). The UCSD team consists of PI Prof. Joanna McKittrick, co-PI Prof. Jan Talbot, graduate students Jinkyu Han and Jae Ik Choi and undergraduate research students John Lee, Young Jin Kim and Juliette Micone. The UCSD team is responsible for synthesis and characterization of phosphors (McKittrick) and the electrophoretic deposition of phosphors (Talbot). The OS team consists of co-PI Dr. Kailash Mishra, and scientists Drs. Mark Hannah, Maria Anc, Dr. Miguel Galvez and Alan Piquette. The OS team is responsible for the identification of phosphor compositions (Mishra), quantum efficiency and thermal stability measurements (Hannah), development of phosphor blends and the fabrication of white-emitting light sources (Anc, Galvez, Piquette).

3.2. RESULTS AND DISCUSSION

Task 1 – Identification of phosphors for excitation in the spectral range of 370-410 nm

We identified 20 Eu^{2+} and 30 Ce^{3+} activated phosphor compositions for near-UV excitation, as shown in Table I.

Table 1. Potential phosphor compositions identified for Ce^{3+} and Eu^{2+} activation
Potential hosts for Eu^{2+} activation

Host	D(A) cm^{-1}	S(A) cm^{-1}	E_a (cm^{-1})	E_a (nm)	E_e (cm^{-1})	E_e (nm)
1 $\alpha\text{-SrSiO}_3$	9610	1663	24390	410	22727	440
2 $\text{Ba}_2\text{Mg}(\text{B}_3\text{O}_6)_2$	8359	2112	25641	390	23529	425

3	Ba ₂ SiO ₄	10959	3240	23041	434	19801	505
4	Ba ₃ Mg(SiO ₄)	9610	1560	24390	410	22830	438
5	BaAl ₁₂ O ₁₉	7684	3589	26316	380	22727	440
6	BaMgAl ₁₀ O ₁₇	9490	2438	24510	408	22072	453
7	Ca ₂ B ₅ SiO ₉ (OH) ₅	8359	3663	25641	390	21978	455
8	Ca ₃ Mg(SiO ₄) ₂	9610	3159	24390	410	21231	471
9	Ca ₃ Mg ₃ (PO ₄) ₄	9610	1454	24390	410	22936	436
10	CaB(OH)SiO ₄	9068	1969	24932	401	22963	435
11	CaMg(SiO ₄)	8529	2115	25471	393	23356	428
12	CaMg(SiO ₄)	12495	3324	21505	465	18181	550
13	LaMgAl ₁₁ O ₁₉ :Ce1	8026	3752	25974	385	22222	450
14	Sr ₂ SiO ₃ Cl ₂	9610	3982	24390	410	20408	490
15	Sr ₂ SiO ₄	8359	5233	25641	390	20408	490
16	Sr ₂ SiO ₄ (2 nd site)	3879	12263	30121	332	17858	560
17	Sr ₃ Mg(SiO ₄) ₂	9610	2560	24390	410	21830	458
18	SrAl ₂ O ₄	8747	2761	25253	396	22492	445
19	SrAl ₂ O ₄	10636	4059	23364	428	19305	518
20	SrMgAl ₁₁ O ₁₇	9309	3186	24691	405	21505	465

Potential hosts for Ce³⁺ activation

	Host	D(A) cm ⁻¹	S(A) cm ⁻¹	E _a (cm ⁻¹)	E _a (nm)	E _e (cm ⁻¹)	E _e (nm)
1	Ba ₂ Lu(BO ₃) ₂ Cl	22313	5568	27027	370	21459	466
2	Ba ₂ Y(BO ₃) ₂ Cl	22313	5568	27027	370	21459	466
3	BaAl ₂ S ₄	23366	3452	25974	385	22522	444
4	BaGa ₂ S ₄	23230	3485	26110	383	22625	442
5	CaAl ₂ S ₄	24088	2525	25252	396	22727	440
6	Ce ₃ (SiS ₄) ₂ Br	23765	4253	25575	391	21322	469
7	Ce ₃ (SiS ₄) ₂ Cl	23567	4809	25773	388	20964	477
8	Cs ₃ Gd ₂ I ₉	23830	2146	25510	392	23364	428
9	GeTaO ₄	24038		25302	395		
10	LaOI	23748	3083	25592	391	22509	444
11	LiYGeO ₄	23284		26056	384		
12	LuOCl	24716		24624	406		
13	Mg ₃ F ₃ BO ₃	24267	3980	25073	399	21093	474
14	NaYGeO ₄	23284		26056	384		
15	SrAl ₁₂ O ₁₉	23816	2900	25524	392	22624	442
16	SrAl ₂ S ₄	24151	3544	25189	397	21645	462
17	SrGa ₂ S ₄	24950	2068	24390	410	22322	448
18	SrLaAlO ₄	24332		25008	400		
19	SrY ₂ O ₄	24529	7332	24811	403	17479	572
20	X1-Gd ₂ SiO ₅	20608	5511	28732	348	23221	431

21	X1-Gd ₂ SiO ₅	23298	4765	26042	384	21277	470
22	X1-Y ₂ SiO ₅	22301	4141	27039	370	22898	437
23	X2-Lu ₂ SiO ₅	21730	2625	27610	362	24985	400
24	X2-Lu ₂ SiO ₅	22744	4951	26596	376	21645	462
25	X2-Y ₂ SiO ₅	21484	3042	27856	359	24814	403
26	X2-Y ₂ SiO ₅	23093	5413	26247	381	20834	480
27	Y ₂ Si ₂ O ₇ N ₂	23699	5232	25641	390	20409	490
28	Y ₃ AlGa ₄ O ₁₂	24480		24860	402		
29	YOI	24815		24525	408		
30	YSiO ₂ N	22313	2335	27027	370	24692	405

Non-radiative energy transfer

Since lanthanide line emitters have been so successfully used in fluorescent lamps and displays, it makes sense to consider them as candidates for nUV LED phosphors. The $4f$ electrons of lanthanide ions in the $3+$ state (Ln^{3+}) are shielded from crystal fields due to the $5s$ and $5p$ electrons of the ligands; hence the crystal field effect is very small. Therefore, each Ln^{3+} is uniquely characterized by its multiplet structure arising from the $4f^n$ configuration, and the corresponding f - f absorption/emission bands are narrow and relatively independent of the host materials. The Ce^{3+} ion is an exception and the broad band emission results from a $4f \rightarrow 5d$ transition. Among the divalent rare earth ions, Sm^{2+} is a line emitter due to transition within the $4f^n$ manifold. Depending on the lanthanide ion, emission could cover the visible spectrum providing appropriate RGB phosphors for higher efficacy and improved color rendering. For example, Tm^{3+} is a known blue emitter, Tb^{3+} , Er^{3+} and Dy^{3+} emit in the green-yellow region, and Pr^{3+} , Sm^{3+} and Eu^{3+} emit in the orange-red region. However, since there are no line-emitting Ln ions except for Tm^{3+} that emit preferentially in the blue, and in most hosts, a significant portion of the Tm^{3+} emission is lost to the infrared, a line-emitting blue component using a Ln^{3+} ion as an activator is not a very practical option.

Many of the green and red line emitting phosphors such as $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{LaPO}_4:\text{Ce}^{3+}$, Tb^{3+} have high quantum efficiencies (>90%) when excited by 254 nm radiation. In the case of Eu^{3+} in Y_2O_3 , the excitation is through the charge transfer band and in $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$, Tb^{3+} is excited through energy transfer from Ce^{3+} that absorbs the 254 nm radiation. The direct excitation of the rare earth ions, in spite of the richness of energy levels in the spectral region of interest, is very weak when compared to $4f \rightarrow 5d$ transitions. The general strategy for fluorescent lamps was to excite Ln^{3+} through the charge transfer transition or $4f \rightarrow 5d$ transitions. Unfortunately, the charge transfer bands of Eu^{3+} in most oxides are located at energies significantly higher than the photon energies from nUV LEDs. For all other lanthanides for which the charge transfer bands have been observed, they occur at higher energies than Eu^{3+} . Therefore, a narrow band phosphor based on a charge transfer band is very unlikely to be found among oxide hosts. Earlier, it was noted that direct excitation through $4f \rightarrow 5d$ bands is almost impossible in oxide hosts other than for Ce^{3+} and Eu^{2+} . Therefore, designing a narrow band phosphor would have to rely on energy transfer from Ce^{3+} or Eu^{2+} , from functional groups such as molybdates or tungstates, or from direct excitation of the host material.

One approach to excite Ln^{3+} is through host excitation where an electron from the valence band is excited directly to the conduction band. Once in the conduction band, the energy can be transferred to a Ln ion. The excited Ln^{3+} then relaxes via an f - f transition to generate the characteristic line emission. The exact mechanism is not well understood. It could be either

capture of electron-hole pairs by the rare earth ion or Dexter-Förster energy transfer. Dy^{3+} is a classic example of a trivalent lanthanide that is often host-sensitized. The Dy^{3+} charge transfer state and $4f \rightarrow 5d$ energies are too large for 254 nm excitation, but in a host such as Ga_2O_3 , there is bandgap absorption (~ 260 nm) and energy transfer leading to line emission. To use host excitation for a nUV approach the bandgap of the host would need to be in the 3.0 eV–3.4 eV range. Furthermore, to be efficient, the host would need to contain a trivalent cation to accommodate an Ln^{3+} activator. Gallium nitride fulfills those two requirements, but is not a good host for large ions due to the small size of Ga^{3+} .

Similar to host excitation is excitation of Ln^{3+} by energy transfer from functional groups such as tungstates and molybdates. In this case, the exciting radiation is absorbed by a functional group within the host and then transferred to the Ln^{3+} activator. Typical tungstate and molybdate absorption bands are in the 250 nm–300 nm region, which again is not useful for a nUV LED lighting solution. However, there are examples of molybdates that absorb in the nUV, transfer that energy to Eu^{3+} , and exhibit red emission (e.g. $\text{Lu}_6\text{MoO}_{12}:\text{Eu}^{3+}$). Unfortunately, the QE values of such materials are typically very low.

The final type of sensitization is the use of other lanthanide ions. In this context, Ce^{3+} and Eu^{2+} are the most important sensitizer ions because their broadband $4f \rightarrow 5d$ transitions can be tuned to nUV energies. The idea is to find a suitable host that can be co-doped with either Ce^{3+} or Eu^{2+} and the Ln^{3+} line emitter(s) of choice. The Ce^{3+} or Eu^{2+} must absorb well in the 380 nm–410 nm region and have an emission band that overlaps with at least one of the $f \rightarrow f$ transitions in a given Ln^{3+} line emitter; preferably in the blue (~ 400 nm–500 nm) range. Fig. 2 shows some of the possible energy levels for various $f \rightarrow f$ transitions in the visible range for four different line emitters (Pr^{3+} , Sm^{3+} , Eu^{3+} and Tb^{3+}). All four of the selected narrowband emitters have at least one transition in the 400 nm–500 nm portion of the spectrum; most have several. If there is overlap between the emission of the $\text{Ce}^{3+}/\text{Eu}^{2+}$ and the Ln^{3+} , there is the possibility of Dexter-Förster non-radiative energy transfer through a multipole-multipole interaction or a short range exchange interaction. These multipole-multipole and exchange interactions are allowed processes and can be quite efficient. An example of a well-known green-emitting fluorescent lamp phosphor that relies on $\text{Ce}^{3+} \rightarrow \text{Ln}^{3+}$ energy transfer is $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$. In terms of a red emitter, Ce^{3+} is typically not a good sensitizer for Eu^{3+} because of metal-to-metal charge transfer quenching, but it has been demonstrated that Ce^{3+} can sensitize Eu^{3+} indirectly through Tb^{3+} , for example in YBO_3 . There have been experiments on $\text{Ce}^{3+} \rightarrow \text{Pr}^{3+}$ energy transfer in $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}, \text{Pr}^{3+}$, but the $\text{Pr}^{3+} \rightarrow \text{Ce}^{3+}$ transfer efficiency was found to be higher than for $\text{Ce}^{3+} \rightarrow \text{Pr}^{3+}$. Similar studies were also done on $\text{Ce}^{3+} \rightarrow \text{Sm}^{3+}$ in a $\text{Y}_3\text{Al}_5\text{O}_{12}$ host, but again, the transfer was not efficient. Even though there are a few instances of $\text{Eu}^{2+} \rightarrow \text{Ln}^{3+}$ such as in $\text{Ca}_{10}\text{K}(\text{PO}_4)_7:\text{Eu}^{2+}, \text{Tb}^{3+}$, $\text{LiSrPO}_4:\text{Eu}^{2+}, \text{Tb}^{3+}$, and $\text{NaSrPO}_4:\text{Eu}^{2+}, \text{Tb}^{3+}$ there are not many examples of Eu^{2+} sensitizing Ln^{3+} ions for narrowband green or, particularly, red emission. Part of the difficulty in using Eu^{2+} as a sensitizer is that the host must be able to accommodate both divalent and trivalent cations simultaneously or there is a charge imbalance. In the specific case of $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ transfer, it is also challenging to get Eu^{2+} and Eu^{3+} to simultaneously exist in the same host.

We investigated the possibility of designing a line emitting phosphor using $\text{Y}_3\text{Al}_5\text{O}_{12}$ as host co-doped with Sm^{3+} and Ce^{3+} . This system was chosen to generate a red emitting phosphor with energy transfer from the Ce^{3+} ions to Sm^{3+} ion. Unfortunately, while we did observe signature emission from the Sm^{3+} ions, it was primarily a result of directly exciting one of the $f \rightarrow f$ transitions and not based on energy transfer from the Ce^{3+} ions. We did not further explore this

system of phosphors for a variety of reasons. First, our main concern was with respect to saturation of the excited state of the rare earth ions due to their long radiative lifetime in the ms range. This could lead to saturation of emission from the trivalent ions at higher excitation energies, and therefore a color shift of the light source. Second, with spectral range of nUV radiation being limited to 380 nm-420 nm, emission and absorption of radiation from both the sensitizer and activator ions being limited to the spectral region from 450 nm-650 nm, it does not allow a large interval on the energy scale to accommodate a Stokes shift of the broad band emitter, and at the same time to meet the requirement of overlap of the emission spectrum of the sensitizer and the absorption spectrum of the activator ions to bring about a successful energy transfer. This problem is somewhat similar to designing a blue emitting phosphor upon excitation by nUV radiation. Finally, the constraint on available time to do a thorough job in this area was not available within the scope of this project. It is a challenging area for phosphor design. Unlike blue emitting LEDs, the nUV sources promise a better chance to design such a phosphor. This calls for long term basic research activities at universities or national labs.

Fig. 2. Energy level diagrams for Pr^{3+} , Sm^{3+} , Eu^{3+} and Tb^{3+} ions based on $\text{LaF}_3:\text{Ln}^{3+}$. For convenience, the transition energies have been converted to the wavelength domain.

Task 2 – Synthesis and optimization of candidate phosphors for quantum efficiency greater than 95%

We have synthesized numerous compositions including silicate, phosphate, oxyfluoride, and oxychloride phosphors activated with Eu^{2+} . Tables 2-4 list some of the blue, green-yellow, and red emitting phosphors that we have synthesized and some of their luminescent characteristics. We have varied the activator concentration and the amounts of alkaline earth elements to optimize both the QE and thermal stability.

Table 2. Luminescence properties of candidate blue emitting phosphors for near UV-LEDs application.

Group	Family	Activator	Composition	Excitation peak (nm)	Excitation at 380-400 nm (%) [*]	Emission peak (nm)
Phosphate	ABPO ₄	Eu^{2+}	LiCaPO ₄	400	100	475
			LiSrPO ₄	350	75	450
			LiBaPO ₄	350	80	480
			NaBaPO ₄	280	75	442
			KCaPO ₄	292	80	473
			KSrPO ₄	325	80	425
			KBaPO ₄	320	80	435
	AB ₂ (PO ₄) ₂	Eu^{2+}	SrMg ₂ (PO ₄) ₂	375	90	420
			SrZn ₂ (PO ₄) ₂	365	85	416
	A ₃ B ₃ (PO ₄) ₄	Eu^{2+}	Ca ₃ Mg ₃ (PO ₄) ₄	300	70	450
	A ₂ P ₂ O ₇	Eu^{2+}	Ca ₂ P ₂ O ₇	330	70	416

			$\text{Sr}_2\text{P}_2\text{O}_7$	300	75	420
	$\text{A}_9\text{B}(\text{PO}_4)_7$	Eu^{2+}	$(\text{Ca}, \text{Mg}, \text{Sr})_9\text{Y}(\text{PO}_4)_7$	280-360	65-85	435-490
Halo-phosphate and silicate	$\text{A}_2\text{PO}_4\text{Cl}$	Eu^{2+}	$\text{Ca}_2\text{PO}_4\text{Cl}$	360	85	454
	$\text{A}_5(\text{PO}_4)_3\text{Cl}$	Eu^{2+}	$\text{Sr}_5(\text{PO}_4)_3\text{Cl}$	345	90	445
			$\text{Ca}_{4.47}\text{Mg}_{0.7}(\text{PO}_4)_3\text{Cl}_9$	-	-	453
			$\text{Ca}_5(\text{PO}_4)_3\text{Cl}$	375	90	459
	$\text{A}_3\text{AlO}_4\text{F}$	$\text{Ce}^{3+}(<0.5\%)$	$(\text{Sr}, \text{Ba})_3\text{AlO}_4\text{F}$	400	100	472
	$\text{A}_5\text{SiO}_4\text{Cl}_6$	Eu^{2+}	$\text{Ba}_5\text{SiO}_4\text{Cl}_6$	380	100	440
Silicate	$\text{A}_3\text{MgSi}_2\text{O}_8$	Eu^{2+}	$\text{Ba}_3\text{MgSi}_2\text{O}_8$	330	70	440
			$\text{Sr}_3\text{MgSi}_2\text{O}_8$	330	55	465
			$\text{Ca}_3\text{MgSi}_2\text{O}_8$	375	95	475
	$\text{A}_2\text{MgSi}_2\text{O}_7$	Eu^{2+}	$\text{Sr}_2\text{MgSi}_2\text{O}_7$	365	65	476
	AMgSi_2O_6	Eu^{2+}	$\text{CaMgSi}_2\text{O}_6$	365	75	450
	A_2BSiO_4	Eu^{2+}	$\text{Li}_2\text{CaSiO}_4$	380	100	480
			$\text{Li}_2\text{BaSiO}_4$	350	60	490
	$\text{AB}_2\text{Si}_3\text{O}_{10}$	Ce^{3+}	$\text{BaY}_2\text{Si}_3\text{O}_{10}$	334	30	404

Table 3. Luminescence properties of candidate green-yellow emitting phosphors for near UV-LEDs application.

Group	Family	Activator	Composition	Excitation peak (nm)	Excitation at 380-400nm (%) [*]	Emission peak (nm)
Phosphate	ABPO_4	Eu^{2+}	NaCaPO_4	395	100	505
Halo-silicate and aluminate	$\text{A}_3(\text{SiO}_4)\text{Cl}_2$	Eu^{2+}	$\text{Ca}_3\text{SiO}_4\text{Cl}_2$	368	90	505
	$\text{A}_3\text{AlO}_4\text{F}$	$\text{Ce}^{3+}(>0.5\%)$	$(\text{Sr}, \text{Ba})_3\text{AlO}_4\text{F}$	400	100	502
			$(\text{Sr}, \text{Ca})_3(\text{Al}, \text{Si})\text{O}_{4+z}\text{F}_{1-z}$	405	95	540
	$\text{A}_8\text{B}_2(\text{SiO}_4)_4\text{Cl}_2$	Eu^{2+}	$\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$	365	85	510
			$\text{Ca}_8\text{Zn}(\text{SiO}_4)_4\text{Cl}_2$	450	80	505
Silicate	A_2SiO_4	Eu^{2+}	Ba_2SiO_4	360	95	510
			Sr_2SiO_4	330-380	80-100	545-570
			$(\text{Ba}, \text{Sr})_2\text{SiO}_4$	510-570	80-100	510-570
	$\text{A}_2\text{BSi}_2\text{O}_7$	Eu^{2+}	$\text{Ba}_2\text{MgSi}_2\text{O}_7$	380	100	505
			$\text{Ba}_2\text{ZnSi}_2\text{O}_7$	353	90	500
			$\text{Ca}_2\text{MgSi}_2\text{O}_7$	395	100	541
	A_2BSiO_4	Eu^{2+}	$\text{Li}_2\text{SrSiO}_4$	310	90	565
	A_3SiO_5	Ce^{3+}	Sr_3SiO_5	405	95	520
Aluminate	AAI_2O_4	Eu^{2+}	SrAl_2O_4	310	80	517
			BaAl_2O_4	350	75	498
	$\text{A}_4\text{Al}_{12}\text{O}_{25}$	Eu^{2+}	$\text{Sr}_4\text{Al}_{12}\text{O}_{25}$	360	95	495
Borate	$\text{A}_3\text{B}_2\text{O}_6$	Eu^{2+}	$\text{Sr}_3\text{B}_2\text{O}_6$	360	75	578
Nitride and oxynitride	b-SiAlON	Eu^{2+}	$\text{Si}_{6-z}\text{Al}_z\text{O}_x\text{N}_{8-z}$	300	80	535
	$\text{ASi}_2\text{O}_2\text{N}_2$	Eu^{2+}	$\text{SrSi}_2\text{O}_2\text{N}_2$	390	100	570
			$\text{CaSi}_2\text{O}_2\text{N}_2$	350	95	560
			$\text{BaSi}_2\text{O}_2\text{N}_2$	300	80	500
			$(\text{Sr}, \text{Ca})\text{Si}_2\text{O}_2\text{N}_2$	350-390	80-100	538-555
			$(\text{Sr}, \text{Ba})\text{Si}_2\text{O}_2\text{N}_2$	300-390	80-100	495-564
	$\text{A}_3\text{Si}_6\text{O}_{12}\text{N}_2$	Ce^{3+}	$\text{Ba}_3\text{Si}_6\text{O}_{12}\text{N}_2$	420	90	527
	$\text{A}_4\text{Si}_2\text{O}_7\text{N}_2$		$\text{Y}_4\text{Si}_2\text{O}_7\text{N}_2$	390	100	500

	$A_2Si_3O_3N_4$		$Y_2Si_3O_3N_4$	390	100	500
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Table 4. Luminescence properties of candidate orange-red emitting phosphors for near UV-LEDs application.

Group	Family	Activator	Composition	Excitation peak (nm)	Excitation at 380-400 nm (%)	Emission peak (nm)
Phosphate	$AB_2(PO_4)_2$	$Eu^{2+}-Mn^{2+}$	$SrMg_2(PO_4)_2$	375	90	675
			$SrZn_2(PO_4)_2$	365	85	613
	$A_3B_3(PO_4)_4$	$Eu^{2+}-Mn^{2+}$	$Ca_3Mg_3(PO_4)_4$	300	70	625
	$A_2P_2O_7$	$Eu^{2+}-Mn^{2+}$	$Ca_2P_2O_7$	330	70	600
			$Sr_2P_2O_7$	300	75	585
	$A_9B(PO_4)_7$	$Eu^{2+}-Mn^{2+}$	$(Ca,Mg,Sr)_9Y(PO_4)_7$	280-360	65-85	632
			$Ca_9La(PO_4)_7$	340	80	635
			$Ca_9Lu(PO_4)_7$	290	50	645
Halo-phosphate	$A_5(PO_4)_3Cl$	$Eu^{2+}-Mn^{2+}$	$Ca_5(PO_4)_3Cl$	375	90	585
Silicate	$A_3MgSi_2O_8$	$Eu^{2+}-Mn^{2+}$	$Ba_3MgSi_2O_8$	330	70	620
			$Sr_3MgSi_2O_8$	330	55	685
	$AMgSi_2O_6$	$Eu^{2+}-Mn^{2+}$	$CaMgSi_2O_6$	365	75	580, 680
	A_3SiO_5	Eu^{2+}	Sr_3SiO_5	400	100	580
			$(Sr,Ba)_3SiO_5$	400	100	580-610
	A_2SiO_4	Eu^{2+}	$(Sr,Ca)_2SiO_4$	400	100	600
Nitride	$A_2Si_5N_8$	Eu^{2+}	$Sr_2Si_5N_8$	400	100	610-680
			$Ca_2Si_5N_8$	395	100	610
			$Ba_2Si_5N_8$	400	100	570-680

Blue-emitting phosphors ($\lambda_{em} = 430-490$ nm)

$ABPO_4$ ($A = Li, Na, K, B = Ca, Sr, Ba$) activated with Eu^{2+} families were studied. $LiCaPO_4:Eu^{2+}$ was found to have superior luminescence properties for near UV-LED application among the $ABPO_4:Eu^{2+}$ family as shown in Fig. 3. The QE of $LiCaPO_4:Eu^{2+}$ is 88% under 400 nm excitation. In addition, $LiCaPO_4:Eu^{2+}$ phosphor has an excellent excitation profile in the near UV range. However, when $LiCaPO_4$ is prepared by solid state reaction appreciable amounts of Li_3PO_4 and $Ca_3(PO_4)_2$ are present as secondary phases. In order to improve the phase purity and synthesize sub-micron sized powders, a sol-gel method with a re-annealing step at 800°C was employed.

The PL emission spectra of both samples excited at 400 nm are shown in Fig. 4. The PL spectra consist of a strong, broad, blue band centered around 470 nm attributed to the allowed $4f^65d \rightarrow 4f^7$ transition of Eu^{2+} . The emission intensity of the submicron sized re-annealed powder is higher than that of the powder annealed only at 1150°C. The QE of the re-annealed powder increased from 62% to ~80%. It is obvious that the phase purity of $Li(Ca_{1-x}Eu_x)PO_4$ plays a crucial role in improving its luminescence properties.

Fig. 3. PL emission spectra of $ABPO_4:Eu^{2+}$ ($A = Li, Na, K, B = Ca, Sr, Ba$) phosphors.

However, we have found $(\text{Sr}_{1-x}\text{Ca}_x)_5(\text{PO}_4)_3\text{Cl}_{1-y}\text{F}_y:\text{Eu}^{2+}$ (SCAP) to be the optimal blue-emitting phosphor, which has a peak emission around 450 nm (Fig. 5). This phosphor is much better suited for these blends as it has much better excitation from 380 nm to 410 nm than our previous blues, and because of its emission peak, SCAP is better for color steering.

Green-yellow-emitting phosphors ($\lambda_{em} = 500\text{-}580$ nm)

$(\text{Ba}_{1-x}\text{Sr}_x)\text{SiO}_4:\text{Eu}^{2+}$ ($0 \leq x \leq 1$) phosphors have excellent thermal stability and a strong green-yellow emission centered around 510-570 nm depending on x . The best composition is for $[\text{Eu}^{2+}] = 3\%$ – a substantial decrease in emission intensity occurs for $[\text{Eu}^{2+}] < 3\%$. Fig. 6(a) shows the effect of x on the emission spectra – the peak is red-shifted as the amount of Sr increases. For these compounds, the PL spectra is composed of emission from Eu from two different sites. One site (Site 1) is coordinated by 10 oxygen ions and another site (Site 2) is surrounded by 9 oxygen ions. The dominant contribution is ascribed to the emission by Site 1. The peak intensity has a maximum for $x = 0.25$. QE measurements were taken on the three samples and the sample with $x = 0$ has the highest at 94%. This is a significant result as we have shown that nanophosphors with QE $\sim 95\%$ has been achieved, one of our milestones for this project. Fig 6b shows QE values for solid-state reacted powders as a function of x . As shown, the highest QE values are for the yellow-emitting composition at $x = 1$ and the green-emitting powder for $x = 0.25$. The difference between the QE values for the nano and micron-sized powders could be due to slight differences in the stoichiometries, due to the two processing conditions.

However, these nanophosphors prepared by sol-gel/Pechini method are severely agglomerated and non-spherical, which may not increase the light extraction efficiency significantly. A novel co-precipitation method using a nonaqueous solvent N,N-dimethylformamide (DMF) has been

Fig. 5. Emission profile of the new SCAP blue phosphor compared to $\text{Ba}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$ and $\text{LiCaPO}_4:\text{Eu}^{2+}$, other blue-emitting phosphors.

Fig. 4. PL emission spectra of $\text{Li}(\text{Ca}_{0.99}\text{Eu}_{0.01})\text{PO}_4$ annealed at 1150°C and re-annealed at 800°C .

developed to produce $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{SiO}_4:\text{Eu}^{2+}$ phosphors with near-spherical, nano/submicron size particles with a narrow size distribution and high quantum efficiency. Fig. 7(a)-(d) shows the SEM micrographs of $(\text{Ba}_{1-x}\text{Sr}_x\text{Eu}_{0.03})_2\text{SiO}_4$ ($x = 0, 0.25, 0.75, 1$) post-annealed at 1100°C . These powders are near-spherical with diameters ranging from 100 nm - 300 nm and are uniformly distributed. The emission peak position as a function of x is shown in Fig. 6(e). The peak position red-shifts as x increases, which is attributed to the crystal field effect. The quantum efficiencies of powders are 82-90% under 400 nm excitation, which is slightly less than for our micron-sized powders (QE $\sim 95\%$), but it is similar

Fig. 6. PL emission intensity of $(\text{Ba}_{1-x}\text{Sr}_x)\text{SiO}_4:\text{Eu}^{2+}$ as a function of x . (a) Sol gel/Pechini chemical synthesis of nanophosphors. Inset shows a particle size of 100-200 nm. $\lambda_{\text{ex}} = 380$ nm. (b) solid state reacted powders.

to commercialized $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ phosphors (QE~85%). These high quantum efficiencies indicate that nano/submicron sized $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ phosphors are very promising green emitters for application in white-emitting near-UV LEDs.

Fig. 7. SEM micrographs of $(\text{Ba}_{1-x}\text{Sr}_x\text{Eu}_{0.03})_2\text{SiO}_4$ for (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.75$, and (d) $x = 1$ and (e) PL emission spectra of $(\text{Ba}_{1-x}\text{Sr}_x\text{Eu}_{0.03})_2\text{SiO}_4$ ($x = 0, 0.25, 0.75$, and 1)

The particle morphology of these phosphors is significantly dependent on the synthetic method. Fig. 8 (a)-(e) shows the SEM micrograph of $(\text{Ba}_{1-x}\text{Sr}_x)\text{SiO}_4:\text{Eu}^{2+}$ at $x = 1$ prepared by hydrothermal, solid-state reaction, combustion, co-precipitation and sol-gel method, respectively. The particle sizes prepared by hydrothermal and co-precipitation are 300-500 nm with nearly spherical shape. However, the morphology prepared by sol-gel and combustion method is needlelike and the length of the both particles is near 1 μm and width is 50 nm. Furthermore, the particles prepared by combustion method are agglomerated. The particles prepared by solid-state reaction are large and very agglomerated: the size is ~ 5 μm. This demonstrates that the

synthetic method plays an important role in determining particle size and morphology. In addition, the quantum efficiencies of these powders range from ~80-95% depending on the synthetic method.

Fig. 8. SEM micrographs of $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ prepared by (a) hydrothermal, (b) solid-state reaction (c) combustion, (d) co-precipitation, and (e) sol-gel method.

Thermal stability is of great importance, since most phosphors degrade when operating at high temperature. Although the estimated temperature of phosphors in a commercially available white-emitting LED is between 150-200°C, this is still enough thermal energy to reduce the QE. We have made thermal stability measurements, as shown in Fig. 9. Samples of $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{SiO}_4:\text{Eu}^{2+}$ and $\text{LiCaPO}_4:\text{Eu}^{2+}$ were cooled to 80K and then warmed to 500K while monitoring the lifetime. At 450K the lifetime of both phosphors retains > 95% of the lifetime at 80K, indicating that these compositions have excellent thermal stability.

When white light is generated from a two or three phosphor blend there will be significant chances for reabsorption of the higher energy photons. This will cause heat to build up in the phosphors and reduce the quantum efficiency. By using multiple activator ions, researchers have tried to avoid this problem with multiple emissions from single phase phosphors.

We can tune the emission of a phosphor by producing solid solutions of compatible host crystals.

Fig. 10(a) and (b) show the emission spectra of Eu^{2+} activated $(\text{KSrPO}_4)_{1-x}(\text{Ba}_2\text{SiO}_4)_x$ (KBPSO) and $(\text{KSrPO}_4)_{1-x}(\text{Sr}_2\text{SiO}_4)_x$ (KSPSO) solid solutions, respectively. As x increases, the ratio of the PL intensity at 490 nm to 430 nm increases. There are two sites in each compound. One site (site 1) is surrounded by 10 oxygen ions and another site (site 2) is surrounded by 9 oxygen ions. In the solid solution, K atoms (site 1) in KSrPO_4 (weak emission) are replaced by Ba or Sr atoms from site 1 (strong emission) in $(\text{Ba,Sr})_2\text{SiO}_4$; and Sr atoms (site 2) in KSrPO_4 (strong emission) are replaced by Ba or Sr atoms from site 2 (weak emission) in $(\text{Ba,Sr})_2\text{SiO}_4$ and thus the intensity at 490 nm increases and intensity at 430 nm decreases with increasing x .

The emission spectra ($\lambda_{\text{ex}} = 380 \text{ nm}$) of KBPSO and KSPSO at $x = 0.1$, which showed the highest emission intensity compared to blue-emitting, sub-micron, $\text{LiCaPO}_4:\text{Eu}^{2+}$ phosphor (QE ~ 80%). While the QE values for KBPSO and KSPSO were not measured, the fluorescence intensities of KBPSO and KSPSO are comparable to that of $\text{LiCaPO}_4:\text{Eu}^{2+}$.

Fig. 9. Lifetime of $\text{LiCaPO}_4:\text{Eu}^{2+}$ and $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}^{2+}$ phosphors as a function on temperature.

Fig. 10. PL emission spectra of Eu²⁺-activated (a) (KSrPO₄)_{1-x}•(Ba₂SiO₄)_x and (b) (KSrPO₄)_{1-x}•(Sr₂SiO₄)_x at various x under 380 nm excitation. The insets are photos showing colors of the corresponding samples, which were taken with a 380 nm emitting UV-LED.

Orange-emitting phosphors ($\lambda_{em} = 580\text{-}610$ nm)

Another promising silicate phosphor was investigated: (Sr_{1-x}Ba_x)₃SiO₅:Eu. Fig. 11(a) is the excitation spectra for various values of x , showing that the phosphor is efficiently excited from 370 nm - 412 nm. Additionally the spectra are flat in that region, indicating that small variations in the emission wavelength of the UV LED will not affect the intensity of the emission. The emission spectra (Fig. 11(b)) illustrate the peaks ranges from 580 to 612 nm depending on x . The QE of these phosphors are 85-95% at $0 \leq x \leq 0.5$, 25-55% at $0.5 \leq x \leq 1$.

Fig. 11. (Sr_{1-x}Ba_x)₃SiO₅:Eu (a) excitation spectra for various values of x and (b) emission spectra for various values of x ($\lambda_{ex} = 380$ nm).

Red-emitting phosphors ($\lambda_{em} = 610-650$ nm)

Seven different red-emitting $(\text{Sr}_{2-x}\text{Eu}_x)\text{Si}_5\text{N}_8$ samples were produced with varying concentration of europium ($0.0075 \leq x \leq 1.00$). Fig. 12 shows the excitation, reflection and emission spectra of $(\text{Sr}_{2-x}\text{Eu}_x)\text{Si}_5\text{N}_8$ at $x = 0.005$. The intensity of the excitation spectrum at ~ 400 nm is excellent and the emission peak is broad and centered around 613 nm, when excited by 380 nm. The QE of these samples was measured at 400 nm excitation, and then plotted. The peak location was also recorded and a plot of peak height was produced (Fig. 13(a)) as well as a plot of QE as a function of Eu concentration (Fig. 13(b)). The highest QE for this phosphor occurs at very low Eu levels. This, however, places the emission peak in the orange range of the spectrum, and limits the usefulness of the powder. To move the emission peak of the phosphor to a more red wavelength, a concentration of europium of around $x = 0.15-0.20$ is needed, which lowers the quantum efficiency to $\sim 75\%$. Thus, a different red phosphor is desirable.

Fig. 12. Measurements on $(\text{Sr}_{2-x}\text{Eu}_x)\text{Si}_5\text{N}_8$: excitation, reflection and emission spectra.

$\text{Ba}_{3-x}\text{Eu}_x\text{Mg}_{1-y}\text{Mn}_y\text{Si}_2\text{O}_8$ was synthesized and examined as a possible alternative. This phosphor produces red light through an energy transfer from Eu^{2+} to Mn^{2+} . This process will prevent the phosphor from absorbing in the green to yellow-orange region of the spectrum and thus will not interfere with the emission of the other phosphors in a blend. Also, as this is a silicate phosphor, no special synthesis techniques are required. Fig. 14(a) shows the excitation, reflection and emission spectra of $\text{Ba}_{3-x}\text{Eu}_x\text{Mg}_{1-y}\text{Mn}_y\text{Si}_2\text{O}_8$. The peak intensity of the excitation spectrum at 270-300 nm does not meet the requirements for our project and the emission peak is broad and centered around 440, 510, 620 nm, when excited by 380 nm. The quantum efficiencies

Fig. 13. (a) The relationship between the percent of europium and the emission peak location and (b) plot showing the relationship between the QE and the Eu concentration for $(\text{Sr}_{2-x}\text{Eu}_x)\text{Si}_5\text{N}_8$.

of these samples are 73% for the samples without Mn^{2+} and 54% with Mn^{2+} . The decrease in QE is attributed to the longer lifetime of the Mn^{2+} . As temperature increases, the red-emission (Mn^{2+}) decreases significantly and the lifetime at 400K is just 50% of that at 80 K as shown in Fig. 14(b). Furthermore, the QE of other red-emitting phosphors with Mn^{2+} or Eu^{3+} activation are reported to be very low (below 5%), thus we have stopped investigating Eu^{3+} and Mn^{2+} phosphor systems.

Fig. 14. (a) Measurements on $\text{Ba}_{3-x}\text{Eu}_x\text{Mg}_{1-y}\text{Mn}_y\text{Si}_2\text{O}_8$: (a) excitation, reflection and emission spectra and (b) the lifetime of red-emission as a function of temperature.

Task 3 – Development of core/shell nanophosphors

Development of luminescence output

We began with $\text{Y}_2\text{SiO}_5:\text{Ce}^{3+},\text{Tb}^{3+}$, a white-emitting phosphor, as a model phosphor core and deposited SiO_2 shells directly on the cores. The phosphor cores were synthesized by a sol gel and modified Pechini method and the shells were deposited by a sol gel method. Fig. 15(a) shows the emission spectra for the core particles along with core/shell particles. The emission intensity increases with the presence of the shells. For a one hour SiO_2 deposition time that resulted in a shell thickness of 15-30 nm, the emission intensity increased by 70% over the bare core particles. Thicker shells (40-60 nm) decrease the emission intensity. SEM micrographs are shown in Fig. 15(b) and (c), where the thin amorphous SiO_2 layer can be observed. This demonstrates two concepts: one is that an inert shell mitigates the surface defects effects, thereby improving the emission intensity and two, there is a critical shell thickness, beyond which the emission intensity decreases (although still better than the bare cores). This result is significant in that we have proven that nanophosphors have the potential to be used in a LED device.

We have shown that $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ is an excellent green-emitting phosphor that has the QE of 90-100%. We investigated the effect of SiO_2 shells on the nanophosphor cores. The emission intensity of the core and core/shell particles is shown in Fig. 15(d). The core particles appear agglomerated (Fig. 14(e)) but the deposition of ~ 40 nm thick SiO_2 shells de-agglomerates the particles (Fig. 14(f)), although there are multiple cores within one particle. However, the core/shell particles are ~ 200 nm in diameter, still small enough to reduce scattering.

Development of chemical and moisture stability

As far as device application is concerned, halides and alkali earth elements in phosphor compositions detrimentally affect the moisture resistance (chemical stability) Fig 16 (a) and (b) shows the comparison of PL spectra of fresh $\text{Ca}_3\text{SiO}_4\text{Cl}_2:\text{Eu}^{2+}$ and $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}^{2+}$ phosphors and the phosphors after soaking in water for 24 h. The emission spectra consist of a single broad band near 520 nm for $\text{Ca}_3\text{SiO}_4\text{Cl}_2:\text{Eu}^{2+}$ and 455 nm for $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}^{2+}$. The PL intensity of both phosphors is significantly decreases after water exposure for 24h. After 24 h water exposure, the intensity of $\text{Ca}_3\text{SiO}_4\text{Cl}_2:\text{Eu}^{2+}$ is 20% and that of $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}^{2+}$ is 70% of that of fresh ones

indicating luminescence properties of both phosphors are easily quenched by the moisture. However, poor moisture stability of these phosphors can be mitigated by SiO₂ shells as shown in Fig 17 (a) and (b). Fig 17 (a) and (b) shows the SEM images and PL spectra of SiO₂ coated on Ca₃SiO₄Cl₂:Eu²⁺ and Ca₂PO₄Cl:Eu²⁺ phosphors. The particle size is over 3 μ m for Ca₃SiO₄Cl₂:Eu²⁺ and 300 nm for Ca₂PO₄Cl:Eu²⁺ and the particles are coated with 15-25 nm SiO₂. Compared to bare core particles, the PL intensity of the core/shell particles after 24 h water exposure is comparable to that of fresh ones indicating the moisture stability of these phosphors can be significantly improved by SiO₂ shells.

Fig. 15. Core/shell nanophosphors: Y₂SiO₅:Ce³⁺, Tb³⁺ / SiO₂; (a) emission spectra ($\lambda_{\text{ex}} = 380$ nm). SEM micrographs showing the amorphous SiO₂ shell around the core particles for shell deposition times of (b) 1 hr and (c) 3 hr. Sr₂SiO₄:Eu²⁺ / SiO₂; (d) emission spectra ($\lambda_{\text{ex}} = 380$ nm) and SEM images (e) the bare cores and (f) core/shell nanophosphors for a SiO₂ deposition time of 2 hr.

Fig 16. The comparison of PL spectra of (a) fresh Ca₃SiO₄Cl₂:Eu²⁺ and after soaking in water for 24 h (b) fresh Ca₂PO₄Cl:Eu²⁺ phosphors and after soaking in water for 24 h.

Fig 17. The PL spectra of fresh $\text{Ca}_3\text{SiO}_4\text{Cl}_2:\text{Eu}^{2+}$ and $\text{Ca}_3\text{SiO}_4\text{Cl}_2:\text{Eu}^{2+}/\text{SiO}_2$ phosphors (b) fresh $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}^{2+}$ and $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}^{2+}/\text{SiO}_2$ phosphors. The core/shell phosphors are measured after soaking in water for 24 h.

Task 4 – Electrophoretic deposition of phosphors

Electrophoretic deposition (EPD) is widely used in the processing of materials and coatings. This technique is suitable for depositing charged particles dispersed in a liquid on a substrate under the force of an applied electric field; a schematic diagram is shown in Fig. 18. There are many factors related to the suspension and the process that affect EPD such as the dissociation of nitrate salts in IPA, the zeta potential of charged particles, the formation of the adhesive agents, and the factors which affect the adhesion strength of the deposited particles.

Our novel high efficiency phosphors were selected for EPD studies: $(\text{SrCa})_2\text{Si}_5\text{N}_8$ (red), Ba_2SiO_4 (green), LiCaPO_4 (blue), $\text{Sr}_{0.75}\text{Ba}_{0.25}\text{SiO}_4$ (yellow) and $(\text{Sr}_{0.75}\text{Ba}_{0.25})_3\text{SiO}_5$ (orange) were deposited on ITO-coated substrates, as shown in Fig. 19. Most phosphor coverage is excellent, demonstrating that EPD is a viable method to produce phosphor layers for the ‘remote phosphor’ design.

For the EPD of individual phosphors, the deposit weight as a function of time is shown in Fig. 20(a) and was converted to thickness as a function of time using the theoretical density of the composition and assuming a packing density of 56 % in Fig. 20(b). The deposition rate was $\sim 1 \mu\text{m}/\text{min}$ for green-, yellow-, and orange-emitting phosphors and $\sim 5 \mu\text{m}/\text{min}$ for red-emitting phosphor, estimated from the thickness of the films. To minimize the settling of $\sim 5\text{-}10 \mu\text{m}$ phosphor particles, the deposition time was limited to 8 min. After 8 min, stratification of the particles in the bath was clearly observed.

Fig. 18. Schematic diagram of the electrophoretic deposition bath.

Fig. 19. Photograph of individual phosphor EPD deposits (2.5×2.5 cm), Eu-activated $\text{Sr}_{2-x}\text{Ca}_x\text{Si}_5\text{N}_8$ (red), Ba_2SiO_4 (green), LiCaPO_4 (blue), $(\text{Sr}_{0.75}\text{Ba}_{0.25})_2\text{SiO}_4$ (yellow) and $(\text{Sr}_{0.5}\text{Ba}_{0.5})_3\text{SiO}_5$ (orange).

Fig. 20. (a) Deposit weight (per 6.45 cm²) and (b) thickness of individual phosphors as a function of time. Eu²⁺-activated $\text{Sr}_{2-x}\text{Ca}_x\text{Si}_5\text{N}_8$ (red – squares), Ba_2SiO_4 (green – triangles), LiCaPO_4 (blue – diamonds), $(\text{Sr}_{0.75}\text{Ba}_{0.25})_2\text{SiO}_4$ (dark yellow – inverted triangles) and $(\text{Sr}_{0.5}\text{Ba}_{0.5})_3\text{SiO}_5$ (orange – circles).

EPD was used to deposit phosphor layers either as a blend or as a sequential deposition, with the goal of obtaining white light with a CCT of ~3000K and a high CRI (>80). Generally, the deposition rate is linear initially, as shown in Fig. 20(a), but as deposition time increased over 8 min, the rate decreased due to the settling of the particles and the decrease of the electric field on the electrode due to the resistance of the film. Specifically, this effect is severe during the deposition of the second layer, since the first layer reduces the electric field strength. Therefore, the range of deposition time was kept between 1 min to 8 min. With OS's suggested phosphor blend compositions, two different blends were deposited on ITO-coated substrates.

Fig. 21 shows the emission results on a CIE chromaticity diagram calculated from PL spectra of a film deposited with two different phosphor blends. Fig. 21(a) shows the results of a three phosphor blend (blue-, yellow- and orange-emitting) with a CCT of 3202 K and CRI of 75. Fig. 21(b) shows the results of a four phosphor blend (blue-, green-, orange- and red-emitting) with a CCT of 3346 K and CRI of 94. The insets show photographs of the generated white light emitted by 365 nm excitation. Both white-emissions are well-situated near the black body locus in the chromaticity diagram. A higher CRI was attained by blending four phosphors as expected, because of the addition of a red-emitting phosphor.

Fig. 21. CIE coordinates and photographs of electrophoretically deposited phosphor blend films ($\lambda_{\text{ex}} = 380 \text{ nm}$). (a) Three phosphor blend: mixture contains blue, 63 wt.%, yellow, 15 wt.% and orange, 22 wt.%. CCT = 3202 K, CRI = 75. (b) Four phosphor blend: mixture contains blue, 70 wt.%, green, 13 wt.%, orange, 5 wt.% and red, 12 wt.%. CCT = 3346 K, CRI = 94. (c) The insets show photographs of the generated white light emitted by $\lambda_{\text{ex}}=365 \text{ nm}$.

These results demonstrate that EPD may be used to fabricate white-emitting phosphor blends with potential application for SSL. Furthermore, the properties of phosphor deposits, correlated color temperature and color rendering index can be manipulated using different phosphor blend compositions.

However, reabsorption of emission colors may occur among the phosphors. Therefore, layered films were investigated and compared to the blended films. Phosphor films were prepared by sequential deposition of red/orange and green/blue compositions to generate white light. The layered films were flipped over and illuminated in this orientation, which showed approximately the same luminescence characteristics. No change in the ratio of the reabsorption of green/blue emission by the red/orange phosphor was found regardless of the deposited order of the layered films. However, the blend deposition was better method due to easier emission color tuning.

Fig. 22(a) shows the results of a red/orange mixture (1 min deposition time) as the first layer and a green/blue mixture (8 min deposition time) as the second layer made by sequential deposition on a CIE chromaticity diagram with a CCT of 3156 K and CRI of 90. The layered film was flipped over and illuminated, which showed approximately the same luminescence characteristics (Fig. 22(b): CCT of 3159 K and CRI of 90). A film with the opposite order, green/blue as the first layer (3 min) and a red/orange as the second layer (5 min), was also fabricated by sequential deposition. The CIE chromaticity diagram in Fig. 23(a) shows a CCT of 2721 K and CRI of 90. The layered film was flipped over and illuminated and was found to have the same luminescence characteristics (Fig. 23(b): CCT of 2719 K and CRI of 90). Thus, two different orders of sequential deposition generated white light.

Fig. 22. Four phosphor blend deposited by sequential electrophoretic deposition. First layer contains red/orange (1:1 wt. ratio), second layer contain green/blue (2:3 wt. ratio). (a) CCT = 3156 K, CRI = 90. (b) CCT = 3159 K, CRI = 90 ($\lambda_{ex} = 380$ nm). (c) 1st layer photograph (looking through the substrate) and 2nd layer photograph (looking on top of the phosphor) at $\lambda_{ex} = 365$ nm.

Fig. 23. Four phosphor blend deposited by sequential electrophoretic deposition. First layer contains green/blue (2:3 wt. ratio), second layer contain red/orange (1:1 wt. ratio). (a) CCT = 2721 K, CRI = 90. (b) CCT = 2719 K, CRI = 90 ($\lambda_{ex} = 380$ nm).

For our goal of remote phosphor configuration with highly efficient phosphors, new blends were deposited by EPD. LiCaPO_4 blue phosphor was replaced with another promising phosphor, SCAP ($(\text{Sr}_{1-x}\text{Ca}_x)_5(\text{PO}_4)_3\text{Cl}_{1-y}\text{F}_y:\text{Eu}^{2+}$) and $\text{Ba}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$. The other phosphors, yellow ($\text{Sr}_{0.75}\text{Ba}_{0.25}\text{SiO}_4:\text{Eu}^{2+}$, green $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$ and red $(\text{Ca}_x\text{Sr}_{1-x-y}\text{Ba}_y)_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ have been added in EPD bath to meet black body locus in CIE diagram.

Two different blends were deposited onto ITO-coated substrates depending on blue phosphor. Fig. 24(a) shows a white converter using four phosphor compositions (blue -, yellow-, green and red-emitting) with CCT of 3259K and CRI of 75 in the case of blue, $\text{Ba}_3\text{MgSi}_2\text{O}_8$. Fig. 24(b) shows a white converter using four phosphor compositions (blue-, yellow-, green and red-emitting) with CCT of 2997K and CRI of 71 in the case of blue, SCAP. The white colors are well situated on the black body locus and white region of the CIE diagram.

Fig. 24. CIE coordinates of 4 phosphors blend EPD (a) 4 phosphors blend with blue, $\text{Ba}_3\text{MgSi}_2\text{O}_8$: B (81%), Y (11%), G (3%) and R (5%), CRI: 75, CCT: 3259 K (b) 4 phosphors blend with blue, SCAP: B (63%), Y (24%), G (6%) and R (7%), CRI: 71, CCT: 2997 K (OS's solid state reacted powders were used. $\text{Ba}_3\text{MgSi}_2\text{O}_8$, $(\text{Sr}_{1-x}\text{Ca}_x)_5(\text{PO}_4)_3\text{Cl}_{1-y}\text{F}_y$, $(\text{Sr}_{0.75}\text{Ba}_{0.25})_2\text{SiO}_4$, $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$ and $(\text{Ca}_x\text{Sr}_{1-x-y}\text{Ba}_y)_2\text{Si}_5\text{N}_8$: blue, blue, yellow, green and red)

There have been few direct comparisons of EPD of nano- and micron-sized particles of the same material. Therefore, EPD of nano-, nano core/ SiO_2 shell and micron-sized $(\text{Ba}_{0.97}\text{Eu}_{0.03})_2\text{SiO}_4$ phosphor particles for application in a near-UV LED-based light source was studied.

$(\text{Ba}_{0.97}\text{Eu}_{0.03})_2\text{SiO}_4$ was prepared by both a solid state reaction and a co-precipitation method, yielding either micron- ($\sim 5 \mu\text{m}$) or nano-sized ($\sim 320 \text{ nm}$) particles, and nano core/ SiO_2 shell particles was prepared by the Stöber process. EPD was performed in IPA or amyl alcohol baths. When a suspension of nano-sized particles in IPA bath was used, a non-uniform and porous film resulted, as shown in Fig. 25. The poor quality of the deposit is attributed to excessive hydrogen evolution during deposition. The increased surface area of nano-sized particle can adsorb a larger quantity of water than for micron-sized particles. With that additional water in the bath, more hydrogen evolution can occur at the cathode due to water electrolysis. Therefore, amyl alcohol, which has low water solubility, was used as the EPD suspension medium instead of IPA.

Fig. 25. A comparison of film quality of micron-sized and nano-sized powders deposited for 10 min from an IPA bath. Photographs of phosphor deposits ($2.5 \times 2.5 \text{ cm}^2$ excited by 365 nm) of (a) micron- and (b) nano-sized particles. Cross-sectional SEM micrographs of (c) micron- (d) nano-sized particles.

The deposit weight and thickness deposits of nano- and micron-sized particles from a bath of amyl alcohol as a function of time are shown in Fig. 26.

Fig. 26. (a) Deposit weight (per 6.25 cm^2) and (b) thickness taken from SEM measurement of individual phosphors as a function of deposition time.

For short times ($< 10 \text{ min}$), the deposit weight and thickness increased linearly with time. The deposit thickness for the micron-sized particle leveled to $26 \mu\text{m}$ at 15 min, whereas the deposit thickness of nano-sized particle plateaued at $33 \mu\text{m}$ at $\sim 30 \text{ min}$. However, the thickness of core/shell nano-sized particles kept increasing to 30 min. Fig. 27 shows cross-sectional SEM micrographs of the deposits as a function of deposition time. Nano-, nano core/SiO₂ shell and micron-sized $(\text{Ba}_{0.97}\text{Eu}_{0.03})_2\text{SiO}_4$ phosphors were successfully deposited by electrophoretic deposition in an amyl alcohol bath.

Fig. 27. Cross-sectional SEM micrographs showing the thickness as a function of deposition time: (a) micron-, (b) nano-sized and (c) core/shell nano-sized particles.

The deposited mass, m can be estimated by the Hamaker equation, $m = C_s v_e A_s t$ where C_s is the suspension concentration, v_e is the electrophoretic velocity, A_s is the deposition area, and t is the deposition time. The electrophoretic velocity equals the product of the electrophoretic mobility, μ , and the electric field, E . The Hamaker equation is valid only for short times when C_s and the electric field are assumed to be constant. However, settling, particularly for micron-sized particles, can be significant. The settling velocity v_s , can be estimated by Stokes' law, $v_s =$

$\frac{2(\rho_p - \rho_f)}{9} \frac{gr^2}{\eta}$ where ρ_f is the density of fluid, g is the gravitational acceleration, and r is the radius of a spherical particle. Therefore, a new equation was developed for predicting the deposited mass, considering the change in concentration of particles in the bath from both settling and deposition. The concentration in the suspension may change due to both deposition and settling. From a mass balance, the change in suspension concentration, C_s , due to settling and deposition can be written as $\frac{dC_s}{dt} = -C_s v_s \frac{A}{V} - \frac{1}{V} \frac{dm}{dt}$, where A is the cross-section area of the bath and V is the volume of the bath. However, the loss of concentration associated with the deposition can be considered minimal (~ 0.001 g/L) compared to the initial bath concentration (5 g/L) in our experiments, so the second term can be neglected. After integrating, the time-dependent concentration is $C_s = C_{s,0} \exp\left(-\frac{v_s A}{V} t\right)$, where $C_{s,0}$ = initial bath concentration. By combining this Eqn. with the Hamaker Eqn., a new equation, $m(t) = \frac{C_{s,0} A v_e V}{v_s A} \left[1 - \exp\left(-\frac{v_s A}{V} t\right)\right]$ is obtained. The new equation predicted the deposited mass better. The experimental values for deposited mass as a function of time for nano- and core/shell nano-sized particles showed good agreement with this equation, however not for the micron-sized particles as shown in Fig. 28(a) and (b). This was attributed to vertical particle concentration gradients in the bath. To eliminate these possible gradients, the bath of micron-sized particles was stirred gently, which gave deposit weights in excellent agreement with the predicted ones from a new Eqn. verifying that instabilities occurred in the amyl alcohol bath. The deposited mass for micron-sized particles from an isopropyl alcohol bath that was not stirred showed good agreement with the theoretical values from a new equation as shown in Fig. 28(c), indicating that the concentration gradients did not develop in this bath.

Fig. 28. Plot of experimental and predicted deposit weight as a function of deposition time. (a) nano-sized particles in amyl alcohol bath, (b) micron-sized particles in amyl alcohol bath, (c) micron-sized particles in isopropyl alcohol bath.

Task 5 – Identification of phosphor blends for optimal CRI and CCT

The initial blend modeling began by considering five of the top performing individual phosphors, which ranged from blue to red (see Table 5 and Fig. 29(a)). Simulations were performed using the ColorCalculator software package from OSRAM SYLVANIA. At a given CCT, the simulations were designed to determine the maximum LPW_{vis} value and corresponding CRI, or the maximum CRI and corresponding LPW_{vis} value. Besides providing information about efficacy and color rendering, one of the major outputs of the simulations was identifying how many different phosphors were actually needed to hit the targets. The first simulation was

designed to estimate the maximum LPW_{vis} values versus CCT using the phosphors listed in Table 5. The following constraints were used for the simulation: CCT = variable (100K increments with a 100K window), CRI ≥ 80 , $|\Delta(uv)| \leq 0.004$, and between 3 and 5 of the phosphor must be used. The results are shown in Fig. 29(b). For each maximum efficacy value, the corresponding CRI was 80 (lowest allowable value from the simulation constraints), which is not unexpected. One of the important results from this simulation study was that the predicted maximum efficacy decreases with higher CCT values.

Fig. 29. (a) Normalized emission spectra of the individual phosphors used for the initial blend simulations. (b) Simulated maximum spectral efficacy versus CCT. The corresponding CRI is given for each point. Not unexpectedly, the CRI value is the lowest allowable based on the constraints.

Since not all of the phosphors were forced into the simulation, there were many blends that fulfilled the criteria that did not contain all five of the phosphors. An interesting result from this simulation is that the red phosphor was not included in any of the max- LPW_{vis} blends. The broadband orange phosphor provided enough red to hit the minimum CRI target.

Based on this range of LPW_{vis} values, an $LPW_{opt,nUV}$ can be estimated. Assuming a Stokes efficiency of 67% (a representative value when going from 390 nm to the λ_{dom} at each CCT) and a conversion/extraction efficiency of 85%, an LPW_{vis} of ~ 320 lm/W translates into an $LPW_{opt,nUV}$ of ~ 182 lm/W. The target efficacy ($LPW_{opt,nUV}$ at 390nm) set forth in the proposal was 175 lm/W. At the actual CCT target of 4100K, the $LPW_{opt,nUV}$ value is estimated to be 179 lm/W. These initial simulations suggested that the efficacy target of 175 $LPW_{opt,nUV}$ could be achieved.

After making several initial blends and testing them, it became apparent that the particular group of phosphors listed in Table 5 has some drawbacks. The blue phosphor (LiCaPO₄:Eu²⁺), peaking at 471 nm, was not blue enough, making it difficult to hit the black body line at CCTs near 4000K. The other leading candidates for blue phosphors were Sr₅(PO₄)₃Cl:Eu²⁺ (SCAP) with an emission peak at 450 nm and Ba₃MgSi₂O₈:Eu²⁺ with a peak at 436 nm. Based primarily on efficiency, but also efficacy, considerations, SCAP proved to be a better option. The green phosphor was slightly modified by increasing the Sr-to-Ba ratio to push the peak to 535 nm.

Table 5. Individual phosphors used for the initial blend simulations.	
	Peak Emission Wavelength (nm)
Blue - LiCaPO ₄ :Eu ²⁺	471
Green - (Sr _{0.25} Ba _{0.75}) ₂ SiO ₄ :Eu ²⁺	521
Yellow - (Sr _{0.75} Ba _{0.25}) ₂ SiO ₄ :Eu ²⁺	559
Orange - (Sr _{0.5} Ba _{0.5}) ₃ SiO ₅ :Eu ²⁺	607
Red - (Sr,Ca) ₂ Si ₅ N ₈ :Eu ²⁺	652

Shifting the blue phosphor to a lower wavelength and the green phosphor to a higher wavelength opened a gap in that part of the spectrum, which was filled by the introduction of a different phosphor, $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$ (emission peak at 508 nm). The yellow phosphor performed very well and was not changed in the next iteration. The orange ($(\text{Sr}_{0.5}\text{Ba}_{0.5})_3\text{SiO}_5:\text{Eu}^{2+}$) and red ($(\text{Sr,Ca})_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$) phosphors were replaced by a single orange/red phosphor ($(\text{Sr,Ba})_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$) that had an emission peak located between the two (615 nm).

This new group of five phosphors (see Table 6 and Fig. 30(a)) was used in a second round of spectral simulations. The constraints of the second round of simulations were similar to the first round with the exception that a tighter $\Delta(\text{uv})$ was required. Instead of allowing between ± 0.004 , the acceptable $\Delta(\text{uv})$ values were limited to ± 0.003 . The results of the simulation are shown in Fig. 30(b). With this second set of five phosphors, the simulation predicts a higher maximum LPW_{vis} at each CCT than for the first set of values even with the smaller $\Delta(\text{uv})$ window. Again, with the exception of the 4000K point, the maximum LPW_{vis} values occurred when the CRI was at the lowest allowable level. Using the same method as before, an estimation of the corresponding $\text{LPW}_{\text{opt,nUV}}$ values can be made. Assuming a 67% Stokes efficiency and an 85% conversion/extraction efficiency, the $\text{LPW}_{\text{opt,nUV}}$ at 4100K is 187 lm/W. Again, this indicates that hitting our target of 175 lm/W_{opt,nUV} at a CRI ≥ 80 should be possible with this set of phosphors.

Numerous blends with the phosphors shown in Table 6 were made and tested. As we will show later, the blend that eventually hit our target came from this combination of five phosphors.

Table 6. Individual phosphors used for the initial blend simulations.

	Peak Emission Wavelength (nm)
Blue – $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$	450
Green 1 – $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$	508
Green 2 – $(\text{Sr}_{0.4}\text{Ba}_{0.6})_2\text{SiO}_4:\text{Eu}^{2+}$	535
Yellow – $(\text{Sr}_{0.75}\text{Ba}_{0.25})_2\text{SiO}_4:\text{Eu}^{2+}$	559
Orange/Red – $(\text{Sr,Ba})_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$	615

(a)

(b)

Fig. 30. (a) Normalized emission spectra of the individual phosphors used for the second round of blend simulations. (b) Simulated maximum spectral efficacy versus CCT using the second batch of five phosphors. The corresponding CRI is given for each point.

From our earlier analysis of near-UV phosphors, we chose three candidate blue phosphors, $\text{LiCaPO}_4:\text{Eu}^{2+}$, $\text{Ba}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$ (BAM), and $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$ (SCAP) for application in nUV LEDs. In order to determine the best among them for use in our white light blends they were tested for their conversion efficiency. Three remote phosphor hemispherical domes 2.54 cm in diameter and 1 mm thick were made with 4 weight percent of the phosphor powder mixed with silicone and cured. Once formed these domes were excited with a 380 nm light source using the same experimental settings, and the spectral power distribution for each phosphor was generated. The emission plots were analyzed and the conversion efficiency of each blue option was calculated. The results showed that SCAP has much higher conversion efficiency than the other two phosphors as shown in Fig. 31 and will be used in every white light blend. The peak emission of the phosphors and the FWHM are shown in Table 7 below.

Fig. 31. Spectral power distribution of emitted blue light from UV phosphor conversion layer excited at 380 nm light source.

Table 7. Peak and FWHM emission of the three blue phosphors hemispherical shells excited with 380 nm light source.

Phosphor	Peak Emission (nm)	FWHM (nm)	Conversion Efficiency
$\text{LiCaPO}_4:\text{Eu}^{2+}$	470	45.7	16%
$\text{Ba}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$	436	35.3	13%
$\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$	446	31.8	33%

The emission spectra from different green, yellow, orange and red phosphors were used to simulate the emission properties of white light blends. The simulations lead to a possible phosphor solution for a target lpw of 180 and CRI >80 for a CCT of 4200 K. A dome is then formed using this phosphor blend and the emission profile of the sample is measured in a sphere. The CCT and the departure of the color point from the black body curve are measured. If the sample is observed to be within a three MacAdam ellipse we measure the lumen output of the phosphor converted light, and the total light output from the package to calculate the lpw_{opt} for this configuration. If the sample is off of the black body curve, the blend composition is modified by interpolating the observed data, and new domes are made. This process was repeated until we achieved the desired color point.

We started with a three phosphor blend of SCAP for blue, a yellow phosphor $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, and a red phosphor, $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$. We could not achieve the proper color temperature with this blend. The CRI was sufficiently high, but the lumen output was below our stated goal of 175 lpw_{opt} (Table 8). In order to increase the lumen output, another green phosphor was added to the blend. In the first trials, $\text{CaMg}(\text{SiO}_4)\text{Cl}:\text{Eu}$ was used for this purpose.

Unfortunately, while the CRI improved with the addition of this phosphor, we did not see a significant increase in lpw_{opt} (Table 9). Our next attempt to increase our lumen output was to add a fifth phosphor to the blend. We added a yellow emitting $(Sr_xBa_{1-x})_2SiO_4:Eu^{2+}$ to the blend. While the CRI of these blends still exceeds 80, and CCTs from 3500K all the way up to 4500K could be achieved, we were still short of the target of 175 lpw_{opt} (Table 10).

We therefore dropped the green Lu-garnet phosphor from the mix, and tried to reach our targets with the remaining four phosphors: SCAP, $(Sr_xBa_{1-x})_2SiO_4:Eu^{2+}$, $CaMg(SiO_4)Cl:Eu$, and $Sr_2Si_5N_8:Eu^{2+}$. However this still proved to be the wrong set of phosphors as the lpw values for these blends remained low. Table 11 shows the results of these blends. For our final set of experiments, only the 2-1-4 silicates were used as well as the 2-5-8 nitride for red. With these three phosphors we were able to create a blend with 180 lpw_{opt} and a CRI of 78 (Table 12). Fig. 32 shows the emission spectra of this phosphor blend. While the CRI of this blend was just a little below our target, it achieved results closest to the goal, while the color point remained on the black body locus.

The goals stated in the plan have proven to be very difficult to achieve simultaneously. We can produce very high CRI light, but with limited lumen output (see Table 13). We can also achieve very high lumen output, but with low CRI (see Table 14). In the few cases where we were able to achieve both high lumens and high CRI we were not able to remain on the BBL. This is a problem with LED phosphors with broad emission and excitation bands. Self absorption of radiation, together with the absorption of the emission from short wavelength phosphors by the long wavelength phosphors, produces a very nonlinear process. This makes simulating the systems extremely difficult. A linear interpolation of the blend composition even in the neighborhood of a desired color point fails to produce a desired phosphor blend. This is true for both near-UV and blue LED solid state lighting systems.

Fig. 32. Spectral power distribution from the closest blend to out requirements.

Table 8. Blend results (wt.% of each phosphor) using $Lu_3Al_5O_{12}:Ce^{3+}$ as a yellow phosphor. SCAP = $Sr_5(PO_4)_3Cl:Eu^{2+}$, 2-5-8 $SrSiN = Sr_{2-x}Eu_xSi_5N_8$, distance is amount from black body curve.

SCAP	Lu garnet	2-5-8 SrSiN	CCT	Distance	CRI	LPW_{opt}
73.4	25.0	1.7	3200	1.14e-3	87	114.23
60.5	37.0	2.5	3250	-1.59e-3	89	121.70
73.8	24.6	1.7	3050	1.58e-3	87	118.07

73.8	24.6	1.7	3000	2.46e-3	86	112.23
73.8	24.6	1.7	3050	2.63e-3	87	105.80
61.0	36.6	2.5	3400	-1.05e-3	89	127.07
61.0	36.6	2.5	3400	-4.40e-4	89	121.45
74.5	24.8	0.7	5300	2.26e-2	81	143.51
73.8	24.6	1.7	3050	1.42e-3	87	120.11
62.0	35.9	2.2	3677	-2.50e-4	91	127.19
62.8	35.2	2.1	3800	1.12e-3	90	130.66
63.5	34.3	2.3	3600	-7.04e-3	91	118.63
63.8	34.2	2.0	4000	-9.00e-4	92	128.46
63.8	34.2	2.0	4000	-1.27e-3	91	139.36
63.8	34.2	2.0	3900	-1.27e-3	91	160.37
63.9	34.3	1.8	4400	-7.20e-3	93	142.68
64.9	33.2	1.9	4400	-3.71e-3	93	118.35

Table 9. Blend results (wt.% of each phosphor) with the addition of $\text{CaMg}(\text{SiO}_4)\text{Cl}:\text{Eu}$, which helped increase the CRI but did not improve the lpw_{opt} . SCAP = $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$, 2-5-8 SrSiN = $\text{Sr}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$, distance is amount from black body curve.

SCAP	Lu garnet	$\text{CaMg}(\text{SiO}_4)\text{Cl}$	2-5-8 SrSiN	CCT	Distance	CRI	LPW_{opt}
69.6	27.9	2.6	15.3	4412	-2.87e-3	96	154.49
72.7	24.7	2.7	15.3	4468	-5.72e-3	95	143.83
72.7	24.4	3.0	17	4199	-1.04e-2	93	140.63
74.2	22.8	3.1	17	3826	-1.25e-2	92	153.46
78.4	18.8	2.9	15.3	4561	-1.18e-2	93	153.42

Table 10. Blend results (wt.% of each phosphor) with the addition of a yellow silicate ($(\text{Sr}_x\text{Ba}_{1-x})_2\text{SiO}_4:\text{Eu}^{2+}$) to increase lumens. This helped however lpw_{opt} not high enough. SCAP = $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$, Lu-garnet = $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, 2-5-8 SrSiN = $\text{Sr}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$, distance is amount from black body curve

SCAP	Lu garnet	2-1-4 Silicate	$\text{CaMg}(\text{SiO}_4)\text{Cl}$	2-5-8 SrSiN	CCT	Distance	CRI	LPW_{opt}
57.3	28.6	10.3	2.1	1.8	3550	6.95e-3	79	177.09
59.6	27.1	9.7	1.9	1.7	3541	1.48e-2	77	182.16
59.9	26.9	9.6	1.9	1.7	3721	1.25e-2	78	162.23
60.5	24.2	12.1	2.2	1.0	4212	2.20e-2	73	188.65
61.1	24.4	12.2	1.2	1.0	4108	1.44e-2	74	170.11
63.8	23.0	10.2	2.0	1.0	4410	1.74e-2	77	175.06
68.8	18.4	9.4	1.2	2.1	3448	-5.67e-3	83	153.17
70.1	16.8	8.4	2.5	2.1	3623	-1.46e-3	84	167.62
70.8	17.0	8.8	2.0	1.4	4402	1.40e-3	83	159.59
71.0	17.0	8.8	1.7	1.4	4555	7.62e-4	83	155.15
70.3	16.9	9.8	1.7	1.3	4513	3.84e-3	80	158.20
71.3	16.3	8.1	2.4	1.9	3973	-8.40e-4	85	163.61

71.2	16.2	8.1	2.4	2.1	3816	-3.09e-3	85	160.06
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Table 11. Blend results (wt.% of each phosphor) for a four phosphor blend. Both lpw_{opt} and CRI decreased over the three phosphor blend. SCAP = $Sr_5(PO_4)_3Cl:Eu^{2+}$, 2-1-4 silicate = $(Sr_xBa_{1-x})_2SiO_4:Eu^{2+}$, 2-5-8 SrSiN = $Sr_{2-x}Eu_xSi_5N_8$, distance is amount from black body curve

SCAP	2-1-4 Silicate	CaMg(SiO ₄)Cl	2-5-8 SrSiN	CCT	Distance	CRI	LPW _{opt}
73.7	19.8	5.3	1.2	4300	1.49e-3	74	177.41
73.7	19.2	5.3	1.8	4000	4.30e-3	78	153.97
80.6	11.3	5.6	2.4	3958	-1.19e-2	90	154.12
78.1	15.6	4.7	1.6	3990	-3.50e-3	77	166.78
81.6	11.4	4.9	2.1	4363	-2.79e-3	90	155.06
80.3	12.8	4.8	2.1	4011	-9.79e-3	87	154.92
78.1	15.6	4.7	1.6	2537	-1.19e-2	79	149.07
77.5	17.8	3.1	1.6	2537	-1.19e-2	79	149.07
77.5	17.8	3.1	1.6	3990	-3.47e-3	77	166.78
77.6	17.9	3.1	1.4	4115	-3.25e-3	77	163.31
77.0	18.5	3.1	1.4	4002	2.00e-4	75	167.52
82.2	14.7	2.1	0.9	3900	3.94e-3	73	141.25
82.2	14.7	2.1	0.9	3900	4.08e-3	73	133.62
82.2	14.7	2.1	0.9	3900	3.67e-3	73	134.99
75.7	20.4	2.7	1.2	4000	3.02e-3	72	149.08
75.7	20.4	2.7	1.2	4000	3.14e-3	72	160.11
75.7	20.4	2.7	1.2	4000	3.14e-3	72	185.57
74.8	20.1	2.7	2.4	3200	-5.30e-3	74	166.11
80.9	16.3	1.3	1.5	3000	2.55e-3	69	141.54
81.0	16.3	1.3	1.5	2950	2.81e-3	68	133.20
81.6	16.4	1.3	0.7	3644	9.78e-3	67	153.85
93.7	4.7	1.1	0.5	4000	3.48e-3	80	88.82

Table 12. Blend results (wt.% of each phosphor) for a four phosphor blend. Using only the 2-1-4 silicates, and the 2-5-8 silicon nitride, we were able to achieve excellent results. SCAP = $Sr_5(PO_4)_3Cl:Eu^{2+}$, 2-1-4 silicate = $(Sr_xBa_{1-x})_2SiO_4:Eu^{2+}$, 2-5-8 SrSiN = $Sr_{2-x}Eu_xSi_5N_8$, distance is amount from black body curve.

SCAP	2-1-4 Silicate	2-1-4 Silicate	2-5-8 SrSiN	CCT	Distance	CRI	LPW _{opt}
75.2	22.5		2.3	4300	2.17e-2	72	159.14
81.3	16.3		2.5	4000	5.59e-3	79	154.88
82.8	14.9		2.3	4460	1.50e-3	82	157.64
81.4	14.7	1.6	2.3	4301	8.88e-4	80	168.68
80.1	14.4	3.2	2.2	4184	3.50e-3	78	179.87
80.5	14.5	2.7	2.3	3848	3.20e-3	78	172.86
80.5	14.5	2.7	2.3	4118	2.40e-3	78	168.26

Table 13. The high CRI blends (wt.% of each phosphor); these all show lumen levels below what is required. SCAP = $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$, Lu-garnet = $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, 2-1-4 silicate = $(\text{Sr}_x\text{Ba}_{1-x})_2\text{SiO}_4:\text{Eu}^{2+}$, 2-5-8 SrSiN = $\text{Sr}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$, distance is amount from black body curve.

SCAP	Lu garnet	2-1-4 Silicate	CaMg-(SiO_4)Cl	2-5-8 SrSiN	CCT	Distance	CRI	LPW _{opt}
68.2	27.3		2.5	2.1	4412	-2.87e-3	96	154.49
71.1	24.2		2.6	2.2	4468	-5.72e-3	95	143.83
76.5	18.4		2.8	2.3	4561	-1.18e-2	93	153.42
63.9	34.3			1.8	4400	-7.20e-3	93	142.68
70.9	23.8		2.8	2.4	4199	-1.04e-2	93	140.63
64.9	33.2			1.9	4400	-3.71e-3	93	118.35
72.4	22.3		2.9	2.5	3826	-1.25e-2	92	153.46
63.8	34.2			2.0	4000	-9.00e-4	92	128.46
63.8	34.2			2.0	3900	-1.27e-3	91	160.37
63.8	34.2			2.0	4000	-1.27e-3	91	139.36
62.0	35.9			2.1	3677	-2.50e-4	91	127.19
63.5	34.3			2.3	3600	-7.04e-3	91	118.63
81.6		11.4	4.9	2.1	4363	-2.79e-3	90	155.06
80.6		11.3	5.6	2.4	3958	-1.19e-3	90	154.12
500	280			16	3800	1.12e-3	90	130.66

Table 14. High lumen blends (wt.% of each phosphor). All of these blends have CRI ~ 80. SCAP = $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$, 2-1-4 silicate = $(\text{Sr}_x\text{Ba}_{1-x})_2\text{SiO}_4:\text{Eu}^{2+}$, 2-5-8 SrSiN = $\text{Sr}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$, distance is amount from black body curve.

SCAP	2-1-4 Silicate	Lu garnet	2-1-4 Silicate	CaMg-(SiO_4)Cl	2-5-8 SrSiN	CCT	Distance	CRI	LPW _{opt}
60.5		24.2	12.1	2.2	1.0	4212	2.20e-2	73	188.65
75.7			20.4	2.7	1.2	4000	3.14e-3	72	185.57
59.6		27.1	9.7	1.9	1.7	3541	1.48e-2	77	182.16
80.1	14.4		3.2		2.2	4184	3.50e-3	78	179.87
73.7			19.8	5.3	1.2	4300	1.49e-2	74	177.41
57.3		28.6	10.3	2.1	1.8	3550	6.95e-3	79	177.09
63.8		23.0	10.2	2.0	1.0	4410	1.74e-2	77	175.06

Task 6 – Fabricate LED white-emitting lamp

It is believed that a light source built using nUV LEDs will suffer from less droop than one made from standard blue LEDs. To test this behavior of nUV LEDs, three light sources were built. One light source has 5 nUV dies topped with a hemispherical glass dome of $\frac{3}{4}$ " diameter, another light source was built with 5 OSLO blue packages and another light source with 5 blue Golden Dragon plus packages. Two of these light sources are shown in Fig. 33.

Each light source was placed inside an integrating sphere and was powered at 50mA to 800mA at 50 mA intervals. The measurement used an “instant-on” approach, where the light source was powered and the scan performed immediately, then the LED is turned off. The measured optical power for each light source is shown in Fig. 34(a) and the ratio of these optical

powers compared to a Golden Dragon Plus light kernel is shown in Fig. 36(b). As shown in these figures, the nUV light source is more efficient than the OSLO and Golden Dragon Plus light sources at elevated currents. Drooping is reduced in the nUV dies compared to OSLO dies and the Golden Dragon Plus dies show the most current droop. In terms of output power, when driven at 800mA, the nUV LEDs are 30% more efficient than the GD+ packages and 15% more efficient than the OSLO packages.

Fig. 33. Two light sources with five NUV dies (left) and five GD+(right) packages utilized in this study.

In order to test the effect of binning of the LED chips, two white light solutions were produced, one at 4000K CCT, and the other at 3000K CCT. The spectral power distribution from both solutions was measured, first using a 380nm light kernel, and then a 410 nm light kernel. The CIE coordinates from the emission profiles were plotted and are shown in Fig. 35. The chromaticity coordinates for the 380 nm excitation and for the 410 nm excitation are within 2 MacAdam ellipses for both the 3000K solution and the 4000K solution. Thus, our binning requirements for nUV LEDs are much less stringent than that of standard blue LEDs. For blue LEDs we have a binning requirement of ± 2.5 nm, with near-UV LEDs we have a binning requirement of ± 15 nm.

Fig. 34. (a) Measured optical power versus electrical current for 3 light sources, NUV, OSLO, and GD+ and (b) and the ratio of their respective optical power to the GD+ blue optical power.

The final form of the nUV lamp is shown in Fig. 36 that was used to test and optimize various blends to reach the target performance of 80 CRI and 175 $LPW_{opt,nUV}$ at 4100K. The phosphor blend was applied in a remote configuration in the form of domes as shown as Fig. 36b. We had 24 blends with CCT between 3900K and 4200K, CRI between 72 and 91, and $LPW_{opt,nUV}$ between 133 and 189. Hitting a target point by varying the blend composition could not be achieved using a linear interpolation scheme because of self-absorption from the individual phosphors and re-absorption by one phosphor from another, and the anti-correlation of CRI and efficacy at the targeted CCT. For example, we achieved high CRI blends of 86 and 93 with 137 $LPW_{opt,nUV}$ at 4118K, and 140 $LPW_{opt,nUV}$ at 4199K respectively. The most efficacious blend has a CRI of 73 at 4212K with 189 $LPW_{opt,nUV}$. The best compromise was obtained for two blend compositions giving lamps with (4184 K, CRI 78, 180 $LPW_{opt,nUV}$) and (4118 K, CRI 78, 168 $LPW_{opt,nUV}$).

Fig. 36. Final lamp configuration (a) and sample phosphor domes (b) used for optimizing phosphor blends.

3.3. CONCLUDING REMARKS

From this work we have made several key observations relevant to designing solid state light sources using near-UV LED chips:

- 1) Reduced current droop allows the same light kernel to be used for both a 40W and a 60W replacement bulb. This can be done simply by increasing the drive current for the LEDs without the need to add extra LEDs to increase the light output.
- 2) We found silicates were the most promising phosphor for use with the near-UV LEDs. They produced some of the highest lumen output, with fairly high CRI values.
- 3) The blue phosphor used in the blend has the dominant effect on conversion efficiency since all of the phosphors in the blend will absorb the blue. If the efficiency of the blue phosphor used can be increased we can increase the overall package efficiency. The key to designing a more efficacious light source using nUV LEDs is to develop a very efficient blue emitting phosphor with a peak at 440 nm with a very narrow FWHM of ~ 25 nm and QE > 95 . Because of the required small Stokes shift of > 50 nm, this is not going to be an easy task.
- 4) Another option to designing an efficient light source would be to find green, yellow, and red phosphors that absorb only the near-UV light, and are transparent in the visible. This choice would lead to white body color for the converter element instead of yellow. This is not possible for blue LEDs as the blue emission has to be absorbed by the phosphor blend, the blend will be intrinsically colored. This continues to be an issue with phosphor converted blue LEDs

4. MILESTONES AND SUCCESS CRITERIA

Task 1 – we have identified potential phosphor compositions (20 Eu^{2+} and 30 Ce^{3+}), which are required for our new light source design. Task 2 – we have optimized synthesis conditions for the production of nanophosphor cores with QE $> 94\%$, which is required to reduce scattering, increasing extraction efficiency. Task 3 – we have successfully developed high QE ($\sim 90\%$) core/shell nanophosphors, which are required to improve the QE of the nanophosphor particles. Task 4 – Individual and blended phosphor coatings were prepared by EPD, which is required for the successful integration of the phosphor with the UV-LED. Task 5 – we have identified appropriate mixtures of 3-5 near-UV phosphors with high CCT and CRI, which is required for an optimal light source. Task 6 – we have fabricated a UV-LED with phosphors – success of all of

the above tasks is required for the fabrication of a novel white-light source. Table 15 summarizes our success criteria.

Table 15. Milestones and success criteria

Task	Description	Success metric	1	2	3	4	Met success metric?
1	Identification of phosphors for excitation in the spectral range of 370-410 nm (OS, UCSD)						YES
2	Synthesis and optimization of candidate phosphors for quantum efficiency greater than 95% (OS, UCSD)	QE > 95%	•				YES
3	Development of core/shell nanophosphors (UCSD)	QE same or better than bare phosphor	•	•	•	•	YES
4	Successful development for integrating the phosphor with the LED by electrophoretic deposition (UCSD)	Uniform EPD coverage, controllable thickness for both bare and core/shell nanophosphors	•	•	•	•	YES
5	Development of phosphor blends for white light generation (OS)		•	•	•	•	YES
6	Fabrication of simple white light sources using candidate phosphor blends and LEDs with efficacy near 140 LPW (OS)		•	•	•	•	YES

4.1. Comparison to MYPP plan

A1.3 Down Converters Description: Explore new non-toxic, high-efficiency wavelength conversion materials for improved quantum yield and phosphor conversion efficiency for the purposes of creating warm white LEDs with a particular emphasis on improving spectral efficiency with high color quality and improved thermal stability.

As shown in Table 16, we were on target with the DOE MYPP.

5. DELIVERABLES

Task 1	List of candidate phosphors for optimization including excitation, emission spectra and quantum efficiency (<i>submitted in 2011 and in this report</i>)
Task 2	List of optimized phosphors with excitation and emission spectra and quantum efficiency (<i>submitted in 2012 and this report</i>)
Task 3	A detailed description of the core/shell nanophosphors, with comparisons to bare phosphor powders (<i>submitted in 2011, 2012 and this report</i>)
Task 4	An analysis of the two phosphor integration schemes: remote phosphor or phosphor powders deposited directly on the LED (<i>submitted in this report</i>)
Task 5	Report of phosphor blends describing the blend composition and performance (<i>submitted in 2012 and this report</i>)
Task 6	Final report on performance of the white light source

Table 16. Comparison to DOE MYPP

<i>Metric(s)</i>	<i>2010 Status(es)</i>	<i>2012 Target(s)</i>	<i>Our progress</i>
Quantum yield (25°C) across visible spectrum	95%	95%	95%
Quantum yield (150°C) across visible spectrum	70%	85%	No measurement
Thermal stability across visible spectrum Relative quantum yield at 150°C vs 25°C	85%	90%	No measurement
Ave. conversion efficiency (pc-LEDs)	58%	72%	56% watts 78% photons
Spectral full width half max. (FWHM)	150 nm (red)	< 50 nm (red)	104 nm
Color stability (pc-LEDs)	Color shift 0.012 u 'v' over life	Color shift < 0.004 u 'v' over life	Not tested yet
LER	~ 315 nm	TBD	328

6. PUBLICATIONS AND PRESENTATIONS RESULTING FROM THIS WORK

Publications

1. Han, J.K., J.B. Talbot, J. McKittrick, "Synthesis and photoluminescence properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{SiO}_2$ nano phosphor core/shell particles," ECS Trans., 28, 183 (2010).
2. Han, J.K., G.A. Hirata, J. B. Talbot and J. McKittrick, "Luminescence enhancement of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{Y}_2\text{SiO}_5:\text{Tb}$, Ce core particles with SiO_2 shells," Mater. Sci. & Eng. B, 176 436–441 (2011).
3. Han, J.K., M. Hannah, G.A. Hirata, J.B. Talbot, K.C. Mishra, and J. McKittrick, "Structure dependent luminescence characterization of green–yellow emitting $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ phosphors for near UV LEDs," J. Lumin. 132, 106–110 (2012).
4. Hannah, M.E., A. Piquette, M. Anc, J. McKittrick, J. Talbot, J.K. Han and K. Mishra, "A study of blue emitting phosphors, $\text{ABPO}_4:\text{Eu}^{2+}$ (A=K, Li, Na; B=Ca, Sr, Ba) for UV LEDs," ECS Trans., 41, 19-25 (2012).
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9. Han, J.K., M.E. Hannah, A. Piquette, J.B. Talbot, K.C. Mishra and J. McKittrick "Sol-gel synthesis of single phase, high quantum efficiency $\text{LiCaPO}_4:\text{Eu}^{2+}$ phosphors", J. Solid

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10. Choi, J.I., E. Sluzky, M. Anc, A. Piquette, M.E. Hannah, K.C. Mishra, J. McKittrick and J.B. Talbot, "EPD of Phosphors for Display and Solid State Lighting Technologies," Key Eng. Mater., 507, 149-153 (2012).
 11. Han, J. K., M. E. Hannah, A. Piquette, J. B. Talbot, K. C. Mishra, and J. McKittrick, "Nano- and submicron sized europium activated silicate phosphors prepared by a modified co-precipitation method." J. Solid State Sci. Technol., 1, R98-R102 (2012).
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 21. Lee, J., J.K. Han, Y.J. Kim, J.B. Talbot, J. McKittrick, "Morphology and particle size dependent luminescence properties of $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ phosphors prepared by various synthetic methods," (in preparation).
 22. Han, J.K., M.E. Hannah, A. Piquette, J. Micone, J.B. Talbot, K.C. Mishra and J. McKittrick, "Particle morphology and luminescence properties of green-emitting $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$ through the hydrothermal reaction route," (in preparation).
 23. Han, J.K., A. Piquette, M. E. Hannah, G. A. Hirata, J. B. Talbot, K. C. Mishra and J. McKittrick, "Sol-gel synthesis of single phase, high quantum efficiency $\text{LiCaPO}_4\text{:Eu}^{2+}$ phosphors," (in preparation)

Invited, keynote presentations and plenary lectures

1. J. McKittrick, J. Tao, G.A. Hirata and E.J. Bosze, "White-emitting phosphors for solid state lighting," 3rd Joint Workshop between UCSD/Korea University, UCSD, Sept. 11, 2009.
2. J. McKittrick, J.B. Talbot and K. Mishra, "Phosphors for near UV-Emitting LEDs for efficacious generation of white light," Dept. of Energy, July 28, 2010, Pittsburgh, PA. (invited).
3. J. McKittrick, J.H. Tao, J.K. Han, M. Hannah, G.A. Hirata, J.B. Talbot and K.C. Mishra, "Novel materials for white-emitting LEDs," 1st International Conference on New Trends in Luminescence and Phosphor Materials, Oct. 4-8, 2010, Hermosillo, Mexico (plenary).
4. J. McKittrick, J.K. Han, J.B. Talbot and K.C. Mishra, "Phosphors for near UV-Emitting LEDs for efficacious generation of white light," Department of Energy R&D Workshop, Feb. 2, 2011, San Diego, CA.
5. J. McKittrick, "Synthesis and characterization of phosphors for near UV LED applications," International Conference on Luminescence and Applications, Feb. 12, 2012, Hyderabad, India (keynote).
6. J. McKittrick, J. Han, J.I. Choi, J.B. Talbot, "Effect of powder synthesis and processing on luminescence properties," The Minerals, Metals & Materials Society Meeting, March 11-15, 2012, Orlando, FL. (invited).
7. J. McKittrick, "The challenges of fabricating nanocrystalline luminescent materials," 1st International Symposium on Nanoscience and Nanomaterials, March 16, 2012, Ensenada, Baja California, Mexico (plenary).
8. J.B. Talbot, J.K. Han, J.I. Choi and J. McKittrick, "Development of efficient solid state lighting materials," 243rd American Chemical Society National Meeting, March 28, 2012, San Diego, CA (invited)
9. J. McKittrick, J.K. Han, M. Hannah, J.I. Choi, A. Piquette, M. Anc, J.B. Talbot and K.C. Mishra, "Phosphors for near UV-emitting LEDs for efficacious generation of white light." Department of Energy R&D Workshop, Jan. 31-Feb. 2, 2013, Long Beach, CA.
10. J. McKittrick, Jinkyu Han, Jae Ik Choi and Jan B Talbot, "Rare Earth Activated Oxides for Solid State Lighting," 8th Pacific Rim International Conference on Advanced Materials and Processes, Aug. 8, 2013, Waikoloa, HI (keynote).
11. J. McKittrick, J.K. Han, J.I. Choi and J.B. Talbot, "Solid state lighting: Design and development of phosphors for near UV LEDs," American Chemical Society Annual Meeting, Sept. 9, 2013, Indianapolis, IN (invited).
12. J. McKittrick, J.K. Han, J.I. Choi, M.E. Hannah, A. Piquette, M. Anc, J.B. Talbot, K.C. Mishra, "Development of phosphors for white emitting near UV LEDs," 224th Electrochemical Society Meeting, October 27 – November 1, 2013, San Francisco, CA (invited).

Contributed presentations

1. J.K. Han, J.B. Talbot and J. McKittrick, "Synthesis of nano core/shell phosphor particles with cores of the luminescent material," Materials Research Society Spring Meeting, San Francisco, CA, April 7, 2010.
2. J.K. Han, J.B. Talbot and J. McKittrick, "Nanophosphor core/shell luminescent properties," UCSD Jacobs School of Engineering Research Expo, April 15, 2010.

3. J.K. Han, J.B. Talbot and J. McKittrick, "Synthesis and photoluminescence properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{SiO}_2$, $\text{Y}_2\text{SiO}_5:\text{Ce}$, Tb/SiO_2 nanophosphor core/shell particles," The 217th Electrochemical Society Meeting, Vancouver, BC, Canada, April 25-29, 2010.
4. J.K. Han, G. Hirata, J. Talbot and J. McKittrick, "Core/shell nanophosphors for LED lighting," 7th Pacific Rim International Conference on Advanced Materials and Processing, Aug. 5, 2010, Cairns, Australia.
5. J.K. Han, M. Hannah, G.A. Hirata, J.B. Talbot, K.C. Mishra and J. McKittrick, "Preparation and luminescence characterization of green/yellow-emitting $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ for near UV-LEDs," 1st International Conference on New Trends in Luminescence and Phosphor Materials, Oct. 4-8, 2010, Hermosillo, MX.
6. J.K. Han, M. Hannah, G.A. Hirata, J.B. Talbot, K.C. Mishra and J. McKittrick, "Core/shell phosphors for excitation by near UV radiation," 1st International Conference on New Trends in Luminescence and Phosphor Materials, Oct. 4-8, 2010, Hermosillo, Mexico.
7. D. Cervantes-Vásquez, J.K. Han, G.A. Hirata and J. McKittrick, "White light emission from rare earth activated yttrium silicate nanoparticles covered with silica," 1st International Conference on New Trends in Luminescence and Phosphor Materials, Oct. 4-8, 2010, Hermosillo, Mexico.
8. J. McKittrick, J.H. Tao, J.K. Han, J.B. Talbot, and K.C. Mishra, "Luminescence properties of $\text{Ga}_{1-x}\text{Al}_x\text{N}$ and $\text{Ga}_{1-x-y}\text{Al}_x\text{Dy}_y\text{N}$ powders," 1st International Conference on New Trends in Luminescence and Phosphor Materials, Oct. 4-8, 2010, Hermosillo, Mexico.
9. J. Han, M. Hannah, J.B. Talbot, K.C. Mishra and J. McKittrick, "Phosphors for near UV-emitting LEDs for efficacious generation of white light," Jacobs School of Engineering Research Expo, April 14, 2011, La Jolla, CA.
10. M. Aburto, J. K. Han, G. A. Hirata and J. McKittrick, "Synthesis and characterization of $(\text{Lu}_{1-x-y}\text{Y}_x\text{Ce}_y)_2\text{SiO}_5$ and $(\text{Lu}_{1-m-n}\text{Y}_m\text{Pr}_n)_2\text{SiO}_5$ powders with fast decay time," 16th International Conference on Luminescence, June 26-July 1, 2011, Ann Arbor, MI.
11. J. K. Han, M. Hannah, A. Piquette, J. Micone, G. A. Hirata, J. B. Talbot, K. C. Mishra and J. McKittrick, "Europium activated barium/strontium silicates for near-UV light emitting diode applications," 16th International Conference on Luminescence, June 26-July 1, 2011, Ann Arbor, MI.
12. M. J. Oviedo, J.K. Han, S. Castro, O. Contreras, Z.S. Macedo, G. A. Hirata and J. McKittrick, "Photoluminescence of bismuth germanate phosphors with silica-shell structure," 16th International Conference on Luminescence, June 26-July 1, 2011, Ann Arbor, MI.
13. J. I. Choi, G. A. Hirata, J. B. Talbot, K. C. Mishra and J. McKittrick, "Silicon-based nitride red phosphors for white light emitting diodes (LEDs)," 220th Electrochemical Society Meeting, Oct. 9-11, 2011, Boston, MA.
14. J. K. Han, M. E. Hannah, J. B. Talbot, K. C. Mishra, and J. McKittrick, "High quantum efficiency of $(\text{Ba}_{1-x}\text{Eu}_x)_2\text{SiO}_4$ sub-micron sized green emitting phosphors for near UV-emitting LEDs," 220th Electrochemical Society Meeting, Oct. 9-11, 2011, Boston, MA.
15. M.E. Hannah, A. Piquette, M. Anc, J. McKittrick, J. Talbot, J. K. Han, and K.C. Mishra, "A Study of Blue Emitting Phosphors, $\text{ABPO}_4:\text{Eu}^{2+}$ (A=K, Li, Na; B=Ca, Sr, Ba) for UV LEDs," 220th Electrochemical Society Meeting, Oct. 9-11, 2011, Boston, MA.

16. G. A. Hirata, J. K. Han, M. E. Hannah, J. B. Talbot, K. C. Mishra, and J. McKittrick, "Synthesis and luminescence properties of full-color $(\text{Ba}, \text{Ca}, \text{Sr})_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}, \text{Mn}^{2+}$ phosphors for near UV-Emitting LEDs," 220th Electrochemical Society Meeting, Oct. 9-11, 2011, Boston, MA.
17. J. B. Talbot, J. I. Choi, E. Sluzky, K. C. Mishra and J. McKittrick, "Electrophoretic deposition of phosphors for UV-emitting LEDs," 220th Electrochemical Society Meeting, Oct. 9-11, 2011, Boston, MA.
18. J. McKittrick, J.K. Han, M. Hannah, J.I. Choi, A. Piquette, M. Anc, J.B. Talbot and K.C. Mishra, "Phosphors for near UV-emitting LEDs for efficacious generation of white light." Department of Energy R&D Workshop, Jan. 31-Feb. 2, 2012, Atlanta, GA.
19. J.I. Choi, E. Sluzky, M. Anc, A. Piquette, M.E. Hannah, K.C. Mishra, J.B. Talbot and J. McKittrick, "Electrophoretic deposition of phosphors for white light emitting diodes," Jacobs School of Engineering Research Expo, April 12, 2012, La Jolla, CA.
20. J.K. Han, M. Hannah, A. Piquette, J.B. Talbot, K.C. Mishra and J. McKittrick, "Phosphors for near UV-emitting LEDs for efficacious generation of white light," Jacobs School of Engineering Research Expo, April 12, 2012, La Jolla, CA.
21. N.L.M. Garcia, Y.J. Kim, J. McKittrick and G.A. Hirata Flores, "Luminescent $\text{Gd}_2\text{O}_3:\text{Eu}$ nanospheres synthesized by spray pyrolysis," 5th international Conference on Surfaces, Materials and Vacuum, Sept. 24-28, 2012, Tuxtla Gutiérrez, Chiapas, Mexico.
22. J. K. Han, J. B. Talbot, and J. McKittrick, "Luminescence properties of $(\text{Ba}, \text{Sr})_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}, \text{Mn}^{2+}$," IEEE Photonics Conference, Sept. 26, 2012, Burlingame, CA
23. J.I. Choi, J. McKittrick and J.B. Talbot, "White-emitting solid state lighting by electrophoretic deposition of phosphors," IEEE Photonics Conference, Sept. 26, 2012, Burlingame, CA
24. J. K. Han, M. E. Hannah, A. Piquette, J. B. Talbot, K. C. Mishra, and J. McKittrick, "Single phase, highly efficient $\text{Li}(\text{Ca}_{0.99-x}\text{Sr}_x\text{Eu}_{0.01})\text{PO}_4$ blue emitting phosphors for near UV-emitting LEDs," 222nd Meeting of the Electrochemical Society, October 7-12, 2012, Honolulu, Hawaii.
25. J. I. Choi, M. Anc, A. Piquette, M. E. Hannah, K. C. Mishra, J. B. Talbot and J. McKittrick, "Highly efficient phosphor-converted white light emitting diode (LED) by electrophoretic deposition," 222nd Meeting of the Electrochemical Society, October 7-12, 2012, Honolulu, Hawaii.
26. J.I. Choi, A. Piquette, M.E. Hannah, K.C. Mishra, J.B. Talbot and J. McKittrick, "Synthesis of $\text{Sr}_2\text{Si}_3\text{N}_8:\text{Eu}^{2+}$ red-emitting phosphors for near UV LEDs," 222nd Meeting of the Electrochemical Society, October 7-12, 2012, Honolulu, Hawaii.
27. Y.J. Kim, J. K. Han, J. Talbot and J. McKittrick. "Morphology and particle size dependent luminescence property of $\text{Y}_2\text{O}_3:\text{Eu}$ phosphors prepared by various synthetic method," 222nd Meeting of the Electrochemical Society, October 7-12, 2012, Honolulu, Hawaii.
28. J. K. Han, M. E. Hannah, A. Piquette, J. B. Talbot, K. C. Mishra, and J. McKittrick, "Luminescence properties and stability improvement by SiO_2 coating on various promising phosphors for near UV-emitting LEDs," 222nd Meeting of the Electrochemical Society, October 7-12, 2012, Honolulu, Hawaii.

29. J.I. Choi, J.B. Talbot and J. McKittrick, "Electrophoretic deposition of phosphors for near UV LED solid state lighting," Jacobs School of Engineering Research Expo, April 18, 2013, La Jolla, CA.
30. J.I. Choi, M.E. Hannah, A. Piquette, M. Anc, J.B. Talbot, K.C. Mishra, J. McKittrick, "Comparison of electrophoretic deposition of nano- and micron-sized $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$ phosphor particles," 224th Electrochemical Society Meeting, October 27 – November 1, 2013, San Francisco, CA.
31. J. Lee, J.K. Han, J.I. Choi, J.B. Talbot and J. McKittrick, "Effect of synthesis methods on the powder characteristics and luminescence properties of nanophosphors," 224th Electrochemical Society Meeting, October 27 – November 1, 2013, San Francisco, CA.
32. J.K. Han, M.E. Hannah, A. Piquette, J.B. Talbot, K.C. Mishra, J. McKittrick, "Luminescence characteristics of color tunable Eu^{2+} -activated $\text{KSrPO}_4\text{-(Ba,Sr)}_2\text{SiO}_4$ phosphors for near UV light emitting diode applications," 224th Electrochemical Society Meeting, October 27 – November 1, 2013, San Francisco, CA.