Phosphor Systems for Illumination Quality Solid State Lighting Products
Contract# DE-FC26-06NT42934
Final Technical Report

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Executive summary

The objective of this program is to develop phosphor systems that will enable LED lamps with 96 lm/W efficacy at correlated color temperatures, (CCTs) ~3000 K, and color rendering indices (CRI) >80 and 71 lm/W efficacy at CCT<3100 K and CRI~95 using phosphor downconversion of LEDs. This primarily involves the invention and development of new phosphor materials that have improved efficiency and better match the eye sensitivity curves. To meet these requirements, the major accomplishments of this program have been:

- Development of spectral goals for new phosphor development based upon the performance and entitlement of current GE/Lumination phosphors and modification of phosphor design rules to maximize lamp efficiency in LED systems.
- Screening of numerous phase systems for new phosphor compositions and evaluation of potential performance using the spectroscopic capabilities
- Invention and development of six different green, yellow, and orange phosphor compositions that have <20% loss in efficiency at 150°C and match the spectral requirements for both higher (90+) and lower CRI blends that have a high lumen equivalent.
- Lamp testing of all new phosphors after initial optimization. While many phosphors have high quantum efficiency at room and elevated temperatures, this does not ensure long-term stability in LED packages. This testing step was critical in our downselection of phosphor compositions for optimization.
- Composition and synthesis optimization of downselected green, yellow, and orange phosphors to exceed the quantum efficiency of current GE Lumination Vio™ phosphors by ~5% at room temperature and >20% at 150°C.
- Blend development using these new phosphors in order to reach the CCT and CRI requirements with validation and testing of these blends using packages similar to the GE Vio™ package.
- 270 lumen, 3 LED lamps with 82 lm/W efficacy at CCT=3000K, CRI~90 (R₉~80) using 450 nm LEDs with 43% wall plug efficiency (WPE). At 50% WPE, this would translate into 3-chip, warm white lamps with >300 lumens at 91 lm/W. In addition, these lamps reduce the efficacy gap between warm white and cool white LEDs that use phosphor downconversion.
- Lamps using 405 nm LEDs with 20% higher steady-state efficacy in 3-chip Vio™ prototypes when compared to lamps using current Vio™ phosphors. The new phosphors have a 40% higher steady-state efficacy in 6-chip Vio prototypes when compared to the current Vio™ phosphors. These large differences are due to the significantly better high temperature performance of our new phosphors and also show key differences between instantaneous and steady-state measurements.
- Reliability testing of all optimized phosphors developed within this program to at least 2,000 hours with no sign of lumen loss or color shifts for these new phosphor compositions at room temperature testing conditions. For initial compositions and synthesis procedures, we have >10,000 hours of lamp testing in Vio™-like prototypes with no signs of lumen loss or phosphor color shift. We have observed some degradation at high temperature-high humidity conditions for some samples of our new yellow-green phosphor composition as well as phosphors that GE Lumination has independently developed.
- Procedures to protect phosphors from reactions when encapsulated in silicone binders under high temperature-high humidity conditions.

Program milestones

This part of the summary details the progress towards meeting specific program milestones as reflected at the time of the milestone. Please note that the specific data (figures, tables, etc.) referred to in these milestones are shown and more extensively discussed in the detailed technical report that starts on page 10.

Task 1- Determine entitlement for current GE phosphors

List of potential phosphors that meet quantum efficiency (QE) & color requirements (4/2007)

In the Lumination portfolio of violet LED phosphors, the blue/blue-green phosphors based upon Eu^{2+} halophosphates have thermal quenching <10% at 150°C and have the correct emission position and emission FWHM that can meet all requirements for general illumination lighting under 405 nm excitation.

There are deficiencies in the green phosphors with respect to the thermal quenching in that both current Lumination candidates have >20% quenching at 150°C. Our key yellow phosphor also is limited in this respect as well. Finally, our deep red phosphor has virtually no quenching at 150°C but has a relatively slow decay time of ~4 ms, making it weakly susceptible to saturation. Therefore, our focus is on green and yellow-orange phosphors.

Spectral goals (peak position, emission FWHM band) for new phosphor development (4/2007)

These goals have been calculated using GE proprietary software to maximize luminosity (matching eye sensitivity) at given CRIs. In general, the CRI/luminosity are not nearly as sensitive for the position/FWHM of the green phosphor as it is for the yellow-orange. As the yellow-orange phosphor is shifted to higher wavelengths within this range, the CRI increases to ~93 with the luminosity correspondingly decreasing to ~300 lm/W-rad.

Green spectral goals: λ_{max} =520-545 nm, emission FWHM <80 nm

Yellow-orange spectral goals: λ_{max} =590-620 nm, emission FWHM <70 nm

Refinement of phosphor rules (4/2007)

Phosphor saturation quenching: No changes compared to previous rules: preferable to have 1/e decay times of <1 ms.

Phosphor absorption in the visible: Use energy transfer processes with fast ions to separate absorption and emission.

Phosphor quenching: In systems with Ce-Eu and monovalent charge compensation, it is critical to use systems with high lattice covalency in order to prevent oxidation of Eu^{2+} due to the incorporation of charge compensation. This is possible in nitride/oxynitride compositions.

Quantifying materials for optimization downselection (4/2007)

One of the key decision points within this program is the selection of phosphor compositions for optimization. Using our experience in developing new phosphors for LEDs, we have set additional constraints that need to be met for downselection for optimization:

- Emission spectra matching the spectral requirements given in Task 1.
- Excitation/absorption spectra showing strong absorption at 405 nm (>50% in unoptimized samples).
- Initial screening quantum efficiencies >50% of standard materials.

- <20% loss in quantum efficiency at 150°C under 405 nm excitation either through decay time measurements and/or integrated intensity measurements.

The requirements for thermal quenching will be critical since intrinsic quenching processes can limit high temperature performance. This cannot be removed by synthesis or composition optimization.

Task 2- Develop new phosphor compositions

One phosphor composition for downselection meeting spectral requirements (4/2007)

We developed a new green oxynitride phosphor material (GP1) that met the spectral requirements for green phosphors and had an initial efficiencies of ~75% compared to typical Lumination green phosphors. There is strong absorption at 405 nm and <5% quenching at 150°C. Therefore, this material was our first composition for downselection.

Two compositions (overall) selected for optimization based upon spectral requirements & spectroscopic evaluation (9/2007)

We developed three potential yellow-orange compositions that could meet the spectral requirements detailed above. We initially selected one phosphor composition due to its improved high temperature efficiency. However, there are some issues in the reliability of this phosphor. The other yellow-orange phosphors have significantly better reliability, so our initial yellow-orange phosphor might require significantly more time and effort in optimization versus compositions #2 and #3. However, we believe that we currently have multiple yellow-orange phosphor compositions that can be optimized and meet the requirements for high efficiency LED lighting.

Downselection of red and green phosphor compositions that meet spectral requirements from Task 1 and pass initial spectroscopy tests at UGA for optimization downselection (no photoionization, fast decay time, thermal quenching) (9/2008)

At the end of Year 1 of this program, we had identified one new green phosphor (GP1) and three orange phosphors (denoted as OP1, OP2, and OP3) that could meet spectral requirements as well as having reduced thermal quenching compared to the current phosphors in the Lumination Vio product. In our initial LED testing, we observed significant phosphor reliability issues with GP1 and OP1, halting significant optimization work on these materials. However, the other yellow-orange phosphors (OP2 and OP3) have shown better initial reliability with no losses out to 5000 hours of lamp testing, so our downselection and optimization tasks (Task#3) for orange phosphors have focused on these two compositions.

The reliability issues for GP1 focused the Task#2 work in Year 2 towards green and green-yellow phosphor compositions. To meet these spectral requirements, we first identified a Eu^{2+} -doped halosilicate composition (GP2) within older GE intellectual property whose emission maximum was at ~512 nm with strong excitation from 390-450 nm. Initial samples showed quantum efficiencies of ~65% with thermal quenching of <15% at 150°C, meeting the initial screening requirements. We worked on trying to shift the Eu^{2+} emission maximum to longer wavelengths to improve the blend properties of this material. However, this work was generally unsuccessful so this material was not optimized further.

To meet the green spectral requirements, our screening experiments also gave us a new Ce^{3+} haloaluminosilicate phosphor (GP3). We were able to tune the emission color from the blue-green to the green-yellow through compositional adjustments. Our initial focus was to map out the appropriate compositional space to determine if there are any trade-offs between room temperature quantum efficiency, color, and thermal quenching, and there did not appear to be any significant trade-offs. All of these initial materials had reasonable initial quantum efficiency (>65%), high temperature efficiency (<15% loss at 150°C), and passed initial reliability screening tests.

Task 3 - Synthesis optimization of new phosphor compositions

Improvement in quantum efficiency for one phosphor compositions by >10% (4/2008)

Through modifications in firing conditions and also starting precursors, we have already improved the quantum efficiency of the GP1 composition by >10%. In addition for our OP1, OP2, and OP3 yellow-orange phosphors, we have also determined some key variables, such as the crucible, that play a role in the phase purity and phosphor efficiency.

Optimization of at least one down-selected phosphor compositions from Task 2 with >85% QE (9/2008)

For the OP2 phosphor composition, we have run designed experiments (DoEs) covering the composition (activator ion levels, non-stoichiometry), starting materials, and firing conditions (number of fires, temperature, time, atmosphere, crucible composition, flow rate) for 5-10 g batches of this material. Using the results from these DoEs, we have improved the QE of this material to 82-85%, meeting the milestone of a >85% QE. In addition, we have also synthesized 50 g of phosphor per furnace run of this material without any losses in the efficiency, indicating no initial scale-up issues and allowing for blend development and lamp testing.

Improvement in QE of red and green down-selected phosphor compositions from Task 2 by >10% (4/2009)

Optimization of at least one additional down-selected phosphor compositions from Task 2 with >85% QE (9/2009)

For the GP3 phosphor composition, the largest initial limitation during phosphor optimization was relatively severe Ce^{3+} concentration quenching. Higher Ce^{3+} concentrations shift the emission towards the yellow spectral region at the cost of high temperature efficiency. Once this key parameter was identified, we have fixed the Ce^{3+} concentration within this sample and started our designed experiments around the processing of this material. Our initial improvement was to reduce the number of firing steps from five firings to two firings, which reduced both the sample variability and also improved the quantum efficiency from ~65% to ~77%. Further optimization of this material involving the fluxing and materials precursors has improved the efficiency of this material to >85%, again leading to an absolute QE>85% under 405 nm excitation. This high efficiency is maintained throughout the entire spectral range for this phosphor. We have developed a 50 g scale synthesis for one yellow and green phosphor composition to enable blend development and lamp testing. In addition, we determined some of

the key processing parameters that can limit both phosphor yield and efficiency for larger scale synthesis. This information is necessary to ensure a smooth transfer of this synthesis procedure to GE Lumination.

Task 4 - Incorporate phosphor materials into polymeric binders and composite processing

<5% loss in phosphor QE when incorporating initial compositions into GE Lumination polymer materials (4/2008)

To this point, in our plaque efficiency and phosphor decay time measurements, we have not measured any losses in phosphor efficiency when incorporating these phosphors into the current phosphor binder used in VioTM lamps. While we had phosphor reliability issues with GP1 and OP1, these reliability issues were due to inherent issues within the phosphor powder, not interactions with the silicone matrix.

<5% loss in phosphor QE when incorporating initial blends into GE Lumination polymer materials (4/2009)

We have continued our testing of our new phosphors within GE Lumination phosphor binders and have not seen any issues or additional losses due to the incorporation of these phosphors. However, we do observe some enhanced reactions at high temperature/high humidity for the GE Lumination deep red phosphor when it is incorporated into typical GE Lumination phosphor binders. Consequently, we have started work towards protection and/or coating of this phosphor. In addition, the lamp testing for our new phosphors (OP2, GP3) has not shown any sign of significant lumen loss or color shifts through at least 6,000 hours for initial samples and 1,000 hours for optimized samples. This is further evidence that there is little to no interaction between phosphor binders and silicones that reduce the QE of our new phosphors.

<5% loss in phosphor QE when incorporating final blends into GE Lumination polymer materials (7/2009)

As noted above, we have not measured any phosphor/polymer degradation when incorporating our new phosphors into typical GE Lumination phosphor binders. We have made progress in the protection of the GE Lumination deep red phosphor, and future lamp tests will indicate whether or not this will be sufficient for VioTM-like packages.

Task 5 -Build and evaluate violet LED-based lamps

Phosphor blend development using new phosphors with blend luminosity of 330 lm/W-rad at CRI=80. (4/2008)

Verify CRI/CCT ranges for new blend development. (4/2008)

It is possible to have calculated phosphor blends using GP1 and OP1 that have very interesting spectral characteristics. However, since these phosphors have generally failed our initial reliability testing, we have not considered them within the milestones for this program. With the combination of GP3 and OP2, we are able to reach lumen equivalents of ~320 lm/W-opt at CRIs

of 83 for CCT=3000K. These lumen equivalents values are somewhat lower than our deliverable of 330 lm/W-opt, but this is natural considering that the CRIs are somewhat higher. We can lower this CRI, thereby raising the luminosity, by adding in OP3 to the blend composition, thereby reaching the luminosity of 330 lm/W-opt at CRIs of ~78. In addition, using internal GE Lumination red line emitting phosphors, it is also possible to reach lumen equivalents of 330 lm/W-opt at CCT=3000 K, CRI~90. Finally, when combining these new phosphors with the current materials in the GE Lumination portfolio, our models for spectral blending show that we are able to reach a full range of CCTs at CRIs ranging from 60-95.

Initial testing of new phosphor compositions for package efficiency & accelerated reliability; no loss in lumen output under accelerated reliability. (9/2008)

Package efficiency of optimized phosphor composition >10% vs. current phosphors. (9/2008)

One of the surprises within this program was the extremely poor reliability of some of our new phosphors, in spite of their high QE at room and elevated temperatures. Our initial testing in Vio™-like lamps showed reliability failures for OP1 and GP1 with very strong losses of >10% after <100 hours. This added another milestone in our phosphor downselection selection process to test in-house on powder plaques the initial reliability of new compositions. The next set of phosphors that were down-selected passed our in-house plaque testing procedure at GE-GRC for reliability (unlike OP1 and GP1) before further optimization begun. However, given the importance of reliability (and the relative difficulty to make accurate predictions for long-term behavior), we have put an initial focus for LED testing towards potential reliability issues. Our experience with OP1, GP1, and other phosphors that have failed LED reliability tests has been that factors such as the thickness of the phosphor coating or the phosphor particle size that could play an important role in the phosphor package efficiency are not critical factors in the phosphor reliability tests. Consequently, these factors were not addressed in these initial lamp tests. Our initial tests on OP2 and OP3 have gone out to >5000 hrs of testing in 405 nm packages, and we have observed no evidence for any lumen loss or color shifts for these materials, giving further confidence for downselection. We have also tested GP3 in reliability and have observed no reliability issues at ~8000 hrs of testing using blue LEDs and 5000 hours of testing with Vio LEDs. This testing is primarily for room temperature operation tests, so the positive results from these experiments allowed the team to have the confidence to further optimize these materials.

As noted above, we have not devoted significant resources towards these factors that govern the package efficiency of our new phosphors. However, the Lumination team has developed proprietary functions based upon the phosphor quantum efficiency, absorption, and thermal quenching that have accurately predicted the performance of modifications within the Vio package. Using these functions, we estimate that the steady-state package efficiency of OP2 at will be ~20% higher versus the current Lumination yellow phosphor, and the steady-state package efficiency of GP2 and GP3 will be ~25% higher versus the current Lumination blue-green phosphor. As discussed below, these estimates have been proven out in our lamp testing results.

Package efficiency of individual optimized phosphor compositions and blends 10% greater than current GELcore phosphors (9/2009)

Demonstration of 10% greater package efficiency for new phosphor blends + luminosity of 330 lm/W-rad (9/2009)

Lamp deliverable of >96 lm/W at 3000 K/CRI~80 & >71 lm/W at ~3000 K/CRI~95 when scaled to a 50% EQE LED chip (9/2009).

During Year 3 of this program, we have worked towards making blends and lamp testing of our new phosphors, including making optimized samples of these new phosphors for lamp testing. First, we have worked with blends of GP3 and OP2 as the green and red components and the standard GE Lumination blue phosphor for a tri-phosphor blend using 405 nm LEDs. We initially had to blueshift the color of GP3 through compositional modifications in order to have CRI>80 at CCT~3000 K. With this modification, we were able to achieve 55 lm/W efficacies (instantaneous) at CCT~3200K, CRI~81 using 405 nm LEDs in a three-chip Vio™ package. This is ~10% higher in efficacy when compared to standard Vio™ blends. In addition, while there is some improvement in pulsed measurements, there is an even larger improvement under steady state conditions where these new blends are ~20% higher in efficacy in three-chip Vio™ packages and ~40% higher in efficacy in six-chip Vio™ packages. These improvements are primarily due to the improved high temperature efficiency of these phosphors, since the phosphor temperature in Vio™ packages can reach 110°C and 130°C for three and six chip packages, respectively. In these blends, the blend luminosity is ~320 lm/W-rad, somewhat lower than our initial milestone. However, the enhanced high temperature efficiency offsets the ~3% lower lumen equivalent for the blue/GP3/OP2 blend. Finally, we have also gone through reliability testing for these blends in both room temperature operation (RTOL) and high temperature (85°C), high humidity (85% RH) (HTHH) testing. The OP2 phosphor shows no apparent signs of degradation or color shifts at 10,000 hours in both RTOL and HTHH testing using 3-chip Vio™-like packages. Our initial tests with the GP3 phosphor also have not shown any signs of degradation or color shifts at 7,000 hours in RTOL and HTHH testing. However, when appropriately modifying the composition of the GP3 phosphor to improve the color rendering in phosphor blends using OP2, there appears to be some degradation of this specific GP3 sample under HTHH conditions. We are currently evaluating this further since this result came towards the end of the program.

While the development of these tri-phosphor blends for 405 nm LEDs has been a major focus of this program, the invention of the GP3 family of phosphors with their inherent compositional and spectral flexibility allowed for blend development with 450 nm LEDs. The other main blend involved GP3 and a deep red line emitting phosphor that was internally developed by GE Lumination in combination with 450 nm LEDs. Using these phosphors, we are able to reach the blend luminosity goal of 330 lm/W-rad at CCT=2700-3000 K and CRI=87-92, depending upon the exact LED wavelength. Making a three LED lamp with 450 nm LEDs that have 43% wall plug efficiency (WPE), leads to a 270 lumen lamp with 82 lm/W efficacy at CCT=3000K, CRI~90 (R₉~80). At 50% WPE, this would translate into 3-chip, warm white lamps with >310 lumens at 95 lm/W. Apart from meeting the general program deliverables, these lamps have an efficacy that is ~90% of typical cool white lamps in similar packages, potentially closing the efficacy gap between cool white and warm white LEDs that use only phosphor downconversion.

Detailed technical report

1. Project Objective:

The objective of the project is the development of illumination quality solid state lighting products that have the required color quality to directly replace less efficient incandescent/compact fluorescent lamps. These products are based upon phosphor downconversion of LEDs (pcLEDs), and will be accomplished by developing phosphor systems that efficiently downconvert violet LEDs into white light for very high color rendering index (CRI) and low correlated color temperature (CCT) lamps. At project completion, this project will deliver 1000 lm lamps with:

- 96 lm/W efficacy at CCT~3000 K and CRI>80
- 71 lm/W efficacy at CCT<3100 K and CRI~95.
- Projected end-user price of <\$40/klm.

2. Technical Approach and Work Plan:

There have been significant technical breakthroughs in LED based lighting, leading to commercial lamps using blue LEDs and phosphor downconversion (blue pcLEDs) that have efficiencies >100 lm/W for CCTs>4500 K and CRIs~75. However, efficiency is not the only requirement that needs to be met in general illumination. SSL products must also meet rigorous color requirements:

- Color points on the Planckian blackbody locus to match typical incandescent/halogen lamps
- Very high CRIs to accurately represent colors
- Minimal device-to-device color variation
- >75K color temperature change over the lamp lifetime (~50,000 hrs).

Phosphor downconverted LEDs could be an effective route to meet the color requirements for broad commercial acceptance and large-scale energy savings. Significant market penetration by pcLEDs will not happen unless the phosphor systems are optimized. This presents a materials challenge for the discovery and optimization of new LED phosphor materials. These phosphors must be efficient under intense LED excitation at high temperatures (>100°C) for 50,000 hr lamp lifetimes. In a DOE Core Technology program (contract# DE-FC26-04NT41956), GE and the University of Georgia (UGA) developed prediction tools for maximum phosphor efficiency in LED packages. This program addressed how to improve the phosphor conversion efficiency through:

- Proper selection of activator ions with fast decay times to prevent quenching from intense LED fluxes.
- Host lattice selection to minimize host/activator interactions, primarily activator photoionization, to eliminate phosphor quenching at high temperatures.

This fundamental understanding for phosphor efficiency in pcLEDs led to the downselection of a key yellow phosphor that was optimized within internal GE/Lumination programs. This phosphor when combined with innovative Lumination lamp design and packaging has led to the recently released Vio™ product, using 405 nm LEDs, with efficacies of ~45 lm/W, warm white

CCTs of 3000–4100 K, CRIs from 70-85, and 50,000 hrs lifetimes with no color shift over product life. This is a significant step towards general illumination SSL, but there are still avenues to improve upon the phosphor systems in these lamps. This primarily involves improving the high temperature efficiencies and matching the phosphor blend emission spectra to the eye sensitivity. The results from the prior Core Technology program help guide the development of new phosphors for the next generation of pcLEDs by quantifying the key parameters (Table 1) to optimize phosphor performance in LEDs.

Table 1. General parameters for quenching in LED phosphors

Mechanism for lower conversion efficiency	Fundamental cause	Methods to improve conversion efficiency
Phosphor saturation at high LED fluxes	Relatively slow decay time (>1 ms) of activators	Selection of activators with much shorter decay times.
Strong quenching at elevated temperatures	Energy migration to host lattice defects	Optimized synthesis process to reduce the concentration of defects.
	Photoionization from lowest excited activator states	New compositions with higher metal-ligand covalency.
	Level crossing between lowest excited activator state and ground state	New compositions with reduced expansion in excited state.
Absorption of down-converted light by other phosphors	Strong overlap between emission and excitation/absorption spectra of phosphors within blends	Compositions using energy transfer between sensitizers and activators to separate phosphor emission and excitation bands.

The measurement tools developed in the prior program will help in the downselection of phosphors for optimization by determining the potential entitlement of new materials. The materials development in this program will be combined with system integration at Lumination to develop high efficiency lighting products (Figure 1):

- Understanding the fundamental luminescence properties of current LED phosphors and using our proprietary phosphor blending software to target accelerated achievement of the DOE roadmap goals for warm white LEDs.
- Developing new phosphor materials using the design rules to reduce our overall screening space. We focus activator selection on Ce^{3+} and Eu^{2+} based phosphors and host lattice selection on phosphor hosts with high metal-ligand covalency. $\text{Ce}^{3+}/\text{Eu}^{2+}$ have fast decay times that minimize saturation based quenching due to high violet LED fluxes. The high metal-ligand covalency controls the spectral position of the phosphor emission and maximizes phosphor efficiency at high temperatures and leads to phosphor development based upon nitride, oxynitride, sulfide, halide, and oxyhalide hosts that are not in the typical development path for fluorescent lamps.
- Synthesis and composition optimization using GE's Design for Six Sigma methodology.
- Incorporating new materials into established polymer binders for implementation and commercialization into SSL products.
- Lamp testing and iterative feedback into composition and synthesis design.

Figure 1. Gantt chart with schedule, milestones, & deliverables.

GE-GRC is the prime contractor responsible for management and execution of this program and collaborates with Professor Uwe Happek at the University of Georgia (UGA) and the GE Lumination LLC business unit. UGA team performs spectroscopic analysis of LED phosphors to determine the entitlement of various compositions and the quenching processes. These measurements include time resolved and steady state luminescence measurements from 2-700 K to determine thermally activated luminescence processes and thermoluminescence measurements to determine defect structures. This guides the downselection of compositions for optimization as well as gives potential routes to improve synthesis. GE Lumination will build and test LED lamps using these new phosphors through white light blend development, lamp prototyping, and reliability evaluation. To meet program goals, GE Lumination has extensive prototyping & testing facilities, including a pilot manufacturing line.

3. Program summary

Task 1 - Determine entitlement for current GE/Lumination phosphors in typical Lumination devices using materials selection rules

It is likely that phosphor operating temperatures of >120°C are possible in future versions of Vio™ with improved LED chips. Given this information, we have evaluated the current Lumination phosphors, including those used in Vio™. The major spectral component in Vio™ is from a single yellow Eu²⁺ phosphor. In order to understand the potential entitlement for this phosphor in future Lumination product, Lumination provided GE-GRC with samples of this phosphor with various Eu²⁺ concentrations to understand if any improvements are possible by removing concentration quenching (Table 2). Lower Eu²⁺ levels should minimize energy migration processes, thereby determining if this is important in the high temperature performance of this material.

Table 2. Efficiency measurements for Lumination yellow-orange phosphor with Eu^{2+} level

Phosphor	QE/Abs	I(150 C)/I(RT)	(x,y)
Typical Eu^{2+}	75/84	62	(0.505,0.482)
Lower Eu^{2+}	79/83	62	(0.501,0.483)
Lowest Eu^{2+}	80/76	60	(0.495,0.486)

The results indicate that while modifying the Eu^{2+} concentration can have an effect on the quantum efficiency of this phosphor, the high temperature performance of this material is not significantly affected. This indicates intrinsic quenching processes, such as photoionization or non-radiative level crossing, is the primary cause of the thermal quenching, in agreement with the results obtained by UGA in the previous DOE program. Synthesis optimization will not give phosphors with improved high temperature efficiency. In addition, the current green phosphors ($\lambda_{\text{em}} \sim 520\text{-}530$ nm) in the Lumination portfolio also have strong intrinsic quenching at $T > 100^\circ\text{C}$. Therefore, our primary task will be to develop new green and yellow-orange phosphors with better high temperature performance.

The spectral goals have been calculated in collaboration with Lumination using GE proprietary software to maximize luminosity (match to eye sensitivity) at given CRIs. In general, the CRI/luminosity are not nearly as sensitive for the position/FWHM of the green phosphor, $\lambda_{\text{max}} = 520\text{-}550$ nm, FWHM < 80 nm, as it is for the yellow-orange, $\lambda_{\text{max}} = 590\text{-}620$ nm, FWHM < 70 nm. As the yellow-orange phosphor is shifted to longer wavelengths within this range, the calculated CRI increases to ~ 93 with the luminosity decreasing to ~ 300 lm/W-rad.

To begin our analysis of orange phosphors, we synthesized orange-red Eu^{2+} phosphors to determine their initial optical properties and routes towards improving their compositions/synthesis as well as for design rules for efficient 405 nm LED phosphors. One property that has consistently come up is that most (if not all) of the orange-red emitting Eu^{2+} phosphors have absorption into the green spectral region. This adds a loss process for phosphor blends since the downconversion of re-absorbed blue/green photons will have a quantum efficiency (QE) of less than unity. During manufacturing, this will also affect the color quality of lamps since variations in the phosphor coating will subsequently lead to variations in the amount of blue/green light in the final lamp spectra. These effects have been observed for the phosphors used in VioTM, but are generally weak since the absorption of these phosphors strongly tails off for $\lambda > 480$ nm.

One method to reduce this effect would be to have one ion absorb 405 nm radiation and have it transfer energy to another ion, thereby separating the absorption spectra from the emission spectra. This process can be demonstrated in $\text{Eu}^{2+}\text{-Mn}^{2+}$ phosphors, where there is strong $4f \rightarrow 5d$ absorption by Eu^{2+} and energy transfer via an exchange mechanism to Mn^{2+} . The main drawback of using these phosphors is that the weak oscillator strength of Mn^{2+} gives a slow decay time leading to quenching via saturation processes. However, the basic concept of using energy transfer can be extended to ions with fast decay times to help to separate the absorption and the emission spectra. The most straightforward example would be to use Ce^{3+} as the sensitizer for Eu^{2+} since the $4f \rightarrow 5d$ absorption of Ce^{3+} is at higher energy versus Eu^{2+} , and there is strong spectral overlap between the $5d \rightarrow 4f$ emission of Ce^{3+} and the $\text{Eu}^{2+} 4f^7 \rightarrow 4f^6 5d^1$

absorption, a necessary requirement for energy transfer. In addition, there are no inherent quenching processes between these ions¹. However, there are two major issues with this scheme:

1. If Ce^{3+} and Eu^{2+} replace trivalent ions, then it is likely that the Eu^{2+} luminescence will be strongly quenched at high temperatures. This is due to a reduction in the energy barrier for Eu^{2+} photoionization, a strong intrinsic luminescence quenching process.
2. If Ce^{3+} and Eu^{2+} replace divalent ions, the barrier for Eu^{2+} photoionization should be high. However, charge compensation for Ce^{3+} replacing a divalent host cation could be necessary to optimize the overall efficiency. In typical oxide hosts, the compensation for Ce^{3+} would typically be alkali metals such as Na^+ , K^+ , etc. The addition of alkali ions to Eu^{2+} phosphors can lead to Eu^{3+} incorporation resulting in a severe loss in phosphor efficiency.

Therefore, additional fundamental understanding is necessary to limit the screening for new orange-red compositions. It is known that in nitride compositions, the high covalency from N^{3-} strongly stabilizes Eu^{2+} versus Eu^{3+} , giving phosphors with extremely good performance at high temperatures². The strong stabilization of Eu^{2+} could allow for the additional charge compensation from Ce^{3+} in these systems. We have demonstrated this in a variety of nitride compositions that the addition of alkali-earth ions shows little to no effect on Eu^{2+} efficiency, giving confidence in the potential success of this approach.

UGA also has been addressing some questions towards the ultimate efficiency of phosphors. One point is whether or not quenching is due to photoionization into the host lattice conduction band or due to non-radiative level crossing. One “chemical” method that could be used to potentially check for photoionization is to add in electron trapping ions such as Sm^{3+} and detect whether or not the Sm^{3+} ion traps the electron and converts to Sm^{2+} . We have demonstrated the initial validity of this method in $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$. While this specific material is a model system for studying this process, further work is underway to determine if this method is valid in other materials. UGA has also evaluated a potential high CRI (>80) single white phosphor, based upon garnets doped with Si-N and Ce^{3+} that was developed under GE/Lumination internal programs prior to this program. The inhomogeneous environment for Ce^{3+} leads to the typical Ce^{3+} garnet emission and a redder emission band for Ce^{3+} ions with Si-N in close proximity. In this context, we have found an additional potential limitation regarding the high temperature efficiency of Ce^{3+} phosphors, especially those with red emission bands. Our studies focused upon $\text{Si}^{4+}\text{-N}^{3-}$ doping within the $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) garnet family of materials. The addition of $\text{Si}^{4+}\text{-N}^{3-}$ led to a significant redshift in the Ce^{3+} emission and excitation spectra, leading to a much redder phosphor versus typical YAG phosphors (Figure 2). However, this additional emission band is strongly quenched at high temperatures (Figure 3).

¹ W. Lehmann and F.M. Ryan, J. Electrochem. Soc., **118**, 477 (1971).

² R. Mueller-Mach et al., Physica status solidi (a) **202**, 1727 (2005).

Figure 2. Room temperature emission spectra ($\lambda_{\text{ex}}=470$ nm) of $(\text{Y}_{0.97}\text{Ce}_{0.03})_3\text{Al}_{5-x}\text{Si}_x\text{O}_{12-x}\text{N}_x$

Figure 3. Decay time versus temperature for $(\text{Y}_{0.97}\text{Ce}_{0.03})_3\text{Al}_5\text{O}_{12}$ ($\lambda_{\text{ex}}=470$ nm; $\lambda_{\text{em}}=560$ nm; denoted as YAG) and the lower energy site in $(\text{Y}_{0.97}\text{Ce}_{0.03})_3\text{Al}_{4.9}\text{Si}_{0.1}\text{O}_{11.9}\text{N}_{0.1}$ ($\lambda_{\text{ex}}=520$ nm, $\lambda_{\text{em}}=750$ nm; denoted as YAG-SiN).

There are two assignments to Ce^{3+} emission quenching: Ce^{3+} photoionization and level crossing from the excited $5d^1$ state to the lower energy $4f^1$ states. By measuring the IR-stimulated luminescence (IRSL) after excitation at various wavelengths (a method developed in the previous DOE Core Technology program), we determined the onset for photoionization in these phosphors (Figure 4) is significantly above the energy of the lowest $5d^1$ level, $\sim 19200 \text{ cm}^{-1}$.

Figure 4. Infrared stimulated luminescence (IRSL) intensity versus excitation wavelength for $(Y_{0.97}Ce_{0.03})_3Al_{4.9}Si_{0.1}O_{11.9}N_{0.1}$ at 80 K (closed circles) and room temperature (open circles). The absence of an IRSL signal for low energy excitation is an indication that photoionization does not occur after excitation into the lowest $5d^1$ level of the low and high-energy Ce^{3+} ions.

The apparent absence of photoionization leads to the conclusion of level crossing as the main quenching mechanism for the redder Ce^{3+} emission in YAG-SiN. Since one of the key parameters for level crossing is the energy position of the lowest $Ce^{3+} 5d^1$ level, this puts a limitation on finding red Ce^{3+} phosphors (that have low energy $Ce^{3+} 5d^1$ levels) with high efficiency at elevated temperatures. This is not necessarily a limitation for yellow or green Ce^{3+} phosphors, but caution must be paid to the Stokes shift, since that also plays an important role in luminescence quenching via level crossing. The level-crossing mechanism of quenching has less of an impact for Eu^{2+} because of the reduced Stokes shift for Eu^{2+} emission and also because the $4f^7$ configuration of Eu^{2+} does not have higher energy levels, unlike the spin-orbit split $4f^1$ configuration of Ce^{3+} .

We have published (see Section 5) the initial results from both of these studies to further advance the fundamental understanding for potential LED phosphors.

Milestones from Task 1

List of potential phosphors that can meet quantum efficiency (QE) & color requirements

In the Lumination portfolio of violet LED phosphors, the blue/blue-green phosphors based upon Eu^{2+} halophosphates have thermal quenching <10% at 150°C and have the correct emission position and emission FWHM that can meet all requirements for general illumination lighting.

There are deficiencies in the green phosphors with respect to the thermal quenching in that both candidates have >20% quenching at 150°C. Our key yellow phosphor also is limited in this respect as well. Finally, our deep red phosphor has virtually no quenching at 150°C but has a relatively slow decay time of ~4 ms, making it weakly susceptible to saturation. Therefore, our focus is on green and yellow-orange phosphors.

Spectral goals (peak position, emission FWHM band) for new phosphor development

These goals have been calculated using GE proprietary software to maximize luminosity (optimize with respect to eye sensitivity) at given CRIs. In general, the CRI/luminosity are not nearly as sensitive for the position/FWHM of the green phosphor as it is for the yellow-orange.

As the yellow-orange phosphor is shifted to higher wavelengths within this range, the CRI increases to ~93 with the luminosity correspondingly decreasing to ~300 lm/W-rad.

Green spectral goals: λ_{max} =520-545 nm, emission FWHM <80 nm

Yellow-orange spectral goals: λ_{max} =590-620 nm, emission FWHM <70 nm

Refinement of phosphor rules

Phosphor saturation quenching: No changes compared to previous rules

Phosphor absorption in the visible: Use energy transfer processes with fast ions to separate absorption and emission.

Phosphor quenching: In systems with Ce-Eu-charge compensation, it is critical to use systems with high lattice covalency in order to prevent oxidation of Eu^{2+} due to the incorporation of charge compensation. This is possible in nitride/oxynitride compositions.

General guidelines for optimization

GE has had extensive experience in taking initial phosphor compositions and optimizing their composition and synthesis for performance in a variety of lighting applications. The quenching at high temperatures is the generally the most difficult parameter to improve, since typically thermal quenching can be due to intrinsic processes that cannot be removed by optimized synthesis. On the other hand, we have seen in our prior phosphor development programs, quantum efficiencies can be improved through precursor selection (to remove unwanted impurities), firing schedules (to control crystallinity and anion vacancies), and washing (to remove unwanted secondary phases). Absorption can also improved by fluxing and firing schedules to increase particle sizes. Using this experience, we have set some minimum performance guidelines to downselect materials for further optimization:

- Emission spectra matching the spectral requirements given in Task 1.
- Excitation/absorption spectra showing strong absorption at 405 nm (>50% in unoptimized samples).
- Initial screening quantum efficiencies >50% of standard materials.
- <10% loss in quantum efficiency at 150°C under 405 nm excitation either through decay time measurements and/or integrated intensity measurements.

Task 2 - Develop new phosphor compositions for violet LEDs

Task 3- Synthesis optimization of new phosphor compositions

We have gone through various aspects of Tasks 2-5, including evaluating LED lamps with our initial phosphor samples. Consequently, the organization of this report will group the major results for the best yellow-orange phosphors and green phosphors separately as well describe some of the additional compositional screening experiments.

Yellow-orange phosphors

Compositional screening of yellow-orange phosphors

We initially tested out the concept of Ce^{3+} - Eu^{2+} energy transfer to develop new compositions for lamps based upon violet LEDs. In addition, we initially screen hosts to determine if Ce^{3+} has strong absorption/emission at 405 nm *and* efficient Eu^{2+} luminescence. Using these parameters, we have made orange phosphors (Figure 5) with 1% Ce/Eu using Na^+ as the charge compensating ion.

Figure 5. Representative emission spectra ($\lambda_{\text{ex}}=405$ nm) of new orange phosphor with $\text{Ce}^{3+}/\text{Eu}^{2+}/\text{Na}^+$ doping

From these initial experiments, the presence of Ce^{3+} improves the absorption at 405 nm as expected, and there does not appear to be an intrinsic quenching process through the addition of Ce/Na to the pure Eu phosphor. In addition, this phosphor shows <10% reduction in the average decay time from <20 K to 425 K ($\sim 150^\circ\text{C}$) when measured at UGA. We have also begun to study $\text{Ce}^{3+} \rightarrow \text{Eu}^{2+}$ energy transfer within this material to aid in the overall optimization of these materials. The Ce^{3+} and Eu^{2+} levels are varied in this material, and the decay profile of the Ce^{3+} emission band is analyzed (Figure 6).

Figure 6. Examples of decay profile ($\lambda_{\text{ex}}=394$ nm; $\lambda_{\text{em}}=520$ nm) for new Ce^{3+} - Eu^{2+} orange compositions.

These decay profiles are evidence that the proposed energy transfer process between Ce^{3+} and Eu^{2+} is occurring since there is a faster decay of Ce^{3+} in the presence of Eu^{2+} and the Ce^{3+} decay is faster with higher Eu^{2+} concentration. In addition, there is no apparent concentration quenching between 1%/2% Ce^{3+} , which is also supported by the similar QE and thermal quenching in samples with Ce^{3+} and Eu^{2+} . Finally, the quantum efficiency of these materials is currently equivalent to the yellow phosphor used by Lumination with specific samples that have efficiencies 10% greater than the current yellow phosphor standard. The thermal quenching of these phosphors is <10% at 150°C , which is significantly better than the current yellow phosphor used by Lumination (Figure 7).

Figure 7. Thermal quenching ($\lambda_{\text{ex}}=405$ nm) for best Ce^{3+} - Eu^{2+} orange compositions versus current yellow phosphor.

Taking this concept further, we extended using Ce/Eu to other host lattices, and the current status for these materials is given below (Table 3):

Table 3: Spectral properties of potential orange-yellow phosphors screened within this program

Phosphor	λ_{max}	QE	$I(150^\circ\text{C})/I(\text{RT})$	Absorption
1 (details above)	620 nm	75%	93%	65%
2	605-610 nm	80%	85%	75%
3	595 nm	50%	88%	60%

Given these results, we initially focused on phosphor#1 for compositional optimization and lamp testing. In our new orange compositions, we began screening for aspects that could strongly affect the quantum efficiency of this material. One clear aspect is the crucible in our experiments (Figure 8).

Figure 8. New orange composition fired in Al_2O_3 crucible (left) and Mo crucible (right).

For the same precursor mother batch, it appears that a sintered Al_2O_3 crucible leads to an inhomogeneous sample with lower quantum efficiency versus a high purity Mo crucible. The exact cause for this is under investigation, however, it is also seen that if any part of the phosphor cake is in contact with Al_2O_3 (either in the tube or crucible carrier tray), the quantum efficiency of the phosphor is significantly lower. The consistent synthesis procedure using Mo crucibles allow for initial LED lamp testing in the Lumination Vio package. We initially made the

required quantities of samples for lamp testing for phosphor composition#1 to give critical data for one factor that is difficult to predict, the lumen maintenance of this phosphor.

While the initial performance of these lamps were reasonable given their status within the optimization process, there are some lumen maintenance issues in that these phosphors can lose up to 20% of their intensity after <100 hours of lamp time. These issues show that no assumptions should be made about the phosphor reliability for these new materials, in spite of the fact that these phosphors have high quantum efficiencies at room and elevated temperatures. In addition, this adds another key testing requirement within our optimization process.

We have started to understand the root cause for some of these issues in order to determine the appropriate steps within our optimization. Part of this task involves developing a simple, in-house testing capability for phosphor reliability. We have done this using the violet LED light engines used in the Lumination Vio™ product and our typical plaques that we use for phosphor measurements. We blend our phosphor with a standard phosphor material that has been shown to not degrade after >15,000 hrs of accelerated life testing within the Vio™ product. The second phosphor acts as an internal standard to calibrate for any losses within the new phosphor. Using this testing procedure, we first tested for any interactions between the new phosphors and the silicone binder used to coat the glass domes versus phosphor blends that are pressed into a plaque (Figure 9).

Figure 9. Degradation of orange phosphor#1 within plaque screening setup, without any silicone binder.

We observe no difference in the degradation of orange phosphor#1 with and without silicone binder. Consequently, we also conclude that the degradation is not from an interaction between the phosphor and silicone but is intrinsic to the phosphor itself. In addition, the losses measured in these plaques are in reasonable agreement with the phosphor losses within accelerated LED testing, giving credence to the testing procedure at GRC.

Analysis of the decay profiles of samples before and after irradiation show that additional non-radiative processes are induced in orange phosphor#1 by high intensity LED radiation (Figure 10).

Figure 10. Decay profile of phosphor#1 before and after 24 hrs LED irradiation

This is an initial indication that some type of “color center” that acts as a sink for Eu^{2+} energy transfer has formed in this material after LED irradiation. Consequently, either removing the defect responsible for this “color center” or preventing the formation of this center under LED irradiation will lead to improvements in the performance of this material. Color center formation typically occurs via a photoionization process, where free carriers are created after photoexcitation and is then trapped at host lattice defects. These initial results from reliability testing point to the need for additional optimization parameters. In our initial screening and downselection process, we focused upon initial quantum efficiency as well as the luminescence quenching at high temperatures. We have now added the initial reliability tests as another key testing parameter in our optimization process. Taking this into account, we have begun designed experiments to screen for any key composition or synthesis parameters that can control/improve the reliability of these phosphors. These experiments included:

- Starting source variation with varying impurity levels to determine if any impurities such as Fe play a key role in the reliability. As an example, some of our starting materials have 30-100 ppm of Fe as residual impurities.
- Crucible composition to reduce any potential contamination.
- Firing temperature and atmospheres.
- Charge compensating ions for Ce^{3+} .
- Compositional modifications for alkaline earth components in the phosphor (i.e. Sr^{2+} replacing Ba^{2+} or Ca^{2+} replacing Sr^{2+}). This can modify the position of $4f^N 5d^1$ levels versus the host lattice conduction band that can correspondingly modify the formation of color centers within these materials.

Through this optimization process, to date, we have observed some stronger effects in the compositional modifications (Figure 11) rather than the initial modifications of the synthesis process.

Figure 11. Reduced degradation of modified composition for orange phosphor#1 within plaque screening setup

In parallel to the optimization and spectroscopic evaluation on composition#1, we have also begun reliability evaluation of OP2 and OP3 using our plaque reliability setup. These new materials are significantly more stable under LED irradiation (Figures 12 & 13) and show virtually no change in efficiency after 100 hours of LED irradiation in plaques.

Figure 12. Initial reliability test for phosphor#2 before and after 100 hrs LED irradiation

Figure 13. Initial reliability test for phosphor#3 before and after 100 hrs LED irradiation

Combining this with the initially promising plaque efficiency data and the matching of our spectral requirements developed in Task 1, we had additional options for yellow-orange phosphors with improved efficiency versus current Lumination phosphors. It is estimated that these phosphors could lead to improvements of up to 20% under typical LED operation. However, at this point, we had yellow-orange compositions whose performance could surpass our current yellow-orange phosphor. Based upon these results, we made materials for initial

LED testing at Lumination for longer-term reliability testing, and the initial tests for these phosphors have run for >10,000 hours in typical Vio packages. We have not see any evidence for lumen losses or color shifts in OP2 and OP3 phosphor compositions. Consequently, we undertook additional work to further optimize these phosphor compositions, primarily the OP2 composition since it better matched the spectra requirements defined in Task 1.

Composition and synthesis optimization of OP2 phosphor

This optimization process used designed experiments (DoEs) to conducted to optimize the quantum efficiency (QE), absorbance at 405 nm (ABS), and relative efficiency at 150 C (150QE). We initially started by screening through various starting precursor sources, as was done in Year 1 for OP1 and GP1 and down-selected our initial precursors. It was also recognized that our initial samples of OP2 required higher levels of Eu^{2+} to improve the overall absorption and QE (Table 3) of this material and reduce scattering losses within LED packages. However, this method to increase phosphor absorption also leads to a severe loss in QE (~75% of standard) at a 2% Eu^{2+} level. Therefore, we initially started our first composition DOE by using constant synthesis conditions with a single firing step (Table 4).

Table 4. Initial DoE using a single firing step to understand the effect of Ce^{3+} and Eu^{2+} level on phosphor QE and absorption.

% Ce	% Eu	QE	ABS
3.75	0.25	75	53
0.25	0.25	75	53
2	2	60	79
0.25	3.75	60	88
3.75	3.75	27	80
2.875	1.125	64.5	68
1.125	2.875	69	83.5
2.875	2.875	61	72.7
1.125	1.125	65	71

The initial trends for QE versus $\text{Ce}^{3+}/\text{Eu}^{2+}$ levels were not completely clear, except that extremely high levels of either Ce^{3+} or Eu^{2+} strongly reduce the room temperature QE. This points to additional factors within the synthesis procedure that are dominating factors in the performance of the material. For example, when firing the materials above a specific temperature or for longer times, there is a large (>50%) drop in the quantum efficiency of this material. In addition, we observed some degree of non-uniformity within the phosphor cake, especially in regard to grittiness after grinding with a mortar and pestle. This issue indicates inhomogeneous mixing in these samples. To alleviate some of these issues, we decided to take a two-step firing approach with the sample re-homogenized and ground in between firing steps. Apart from this process change, we also ran an extensive DoE to map out $\text{Ce}^{3+}/\text{Eu}^{2+}$ levels as well as the firing conditions within the furnace (Table 5). The dwell times in Table 5 reflect the total hold times at that temperature (i.e. 4 represents 2 firings each with a dwell time of 2 hours).

Table 5. Second DoE for the optimization of OP2

% Eu	% Ce	temp	dwell	Abs	QE	150QE
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2.625	0.25	Medium-low	4	80.9	85	78.8
2.3	0.15	Medium	8	81.1	79	82.4
2.9	0.35	Medium	8	85.6	70	75.7
2.3	0.15	Low	2	76.1	89	80.2
2.9	0.35	Low	2	80.4	80	78.6
2.9	0.15	Low	8	83.8	86	75.4
2.3	0.35	Low	8	80.4	86	76.3
2.9	0.15	Low	2	80.4	86	76.9
2.3	0.35	Medium-high	2	78.4	83	81.7
2.5	0.15	Medium-low	15	78.6	69	77.6
3.25	0.075	Medium-low	15	82.4	35	65
3.25	0.15	Medium-low	5	82.6	73	74.6
2.5	0.075	Medium-low	5	77.7	55	74.7
2.5	0.15	High	5	79	41	72.6
3.25	0.075	High	5	84.4	62	73.2
3.25	0.15	High	15	87.4	30	57.8
2.5	0.075	High	15	80.1	14	63.2

The results of this DoE show that the QE can be increased significantly by lowering the synthesis temperature and/or shortening the hold time at temperature. Other trends that were observed in these DoEs were that higher Eu^{2+} levels generally decreased the high temperature performance at 150°C versus the room temperature QE. Similar to our previous screening experiments, long hold times and higher synthesis temperatures are detrimental to both room temperature and high temperature QE. Using the results from this DoE, we have initially settled on a firing schedule of two runs at lower firing temperatures with 4 hour long holds, in 2% H_2/N_2 with the phosphor being ground in a mortar and pestle between the two runs to homogenize the product. Using this standard operating procedure, we have been able to reproduce these results with larger batch sizes, enabling the synthesis of ~50 g of these phosphors with virtually identical luminescent properties to the smaller batch samples in the DoEs. The final test for this larger batch sample before extensive lamp testing was to screen for reliability using the plaque testing capabilities at GE-GRC. These samples showed no degradation in our screening experiments (Figure 14) just as in our previous tests with this material. This gives confidence moving forward with extensive studies regarding blends and lamp testing that will occur in Year 3 of this program. We have concluded our initial synthesis optimization of OP1 with >10% improvements in the room temperature quantum efficiency as well as >5% improvements in the plaque absorption. There are some slight losses in the thermal quenching at 150°C versus our initial samples, but they are smaller versus the gains in the other factors. Our next steps will be towards additional optimization based upon the lamp testing of this phosphor. For example, one potential focus in the future (if necessary) would be to optimize the high temperature properties of this material via synthesis modifications to bring the losses at 150°C to <15%.

Figure 14. Plaque reliability testing of optimized orange phosphor made in larger batches.

We have also investigated the synthesis sensitivity of our orange phosphor to understand if there are any additional pathways to improve upon the quantum efficiency of this phosphor. Primarily, we have focused upon potential routes for oxygen contamination of the precursor materials by exposing the precursors to a variety of environments before high temperature firing (Table 6). We find that it is unlikely that unintentional oxygen contamination causes a severe degradation in performance of this orange phosphor.

Mixing condition	Add'l exposure?	QE/ Abs
<0.1 ppm H ₂ O, <3 ppm O ₂	Direct transfer to furnace	82.5/83
<0.1 ppm H ₂ O, <3 ppm O ₂	Flowing N ₂ glove bag for 24 hrs then furnace transfer	84/85
<0.1 ppm H ₂ O, <3 ppm O ₂	Direct transfer to furnace	82.5/84.5
Flowing N ₂ glove bag with precursors in glove bag for 24 hrs	Direct transfer to furnace	84/83

Table 6. Synthesis modifications of our orange phosphor to test for synthesis sensitivity

Green phosphors

Screening and initial optimization of GP1

We have been using high throughput screening (or combinatorial) methods to attempt to accelerate the discovery of new phosphor materials. To do this, we take slurries of powder compounds, dispense given volumes of them in alumina crucibles, and fire these mixtures in different atmospheres. In principle, this allows us to go through and screen within large areas of phase space in single experiments. These samples are initially evaluated for phase identification via XRD and their emission spectra is taken using a 407 nm Kr⁺ laser. Using these methods, we have been able to discover a new potential Eu²⁺ green phosphor in the BaO-Si₃N₄-SiO₂ oxynitride system that can be excited by 405 nm LEDs (Figure 15).

Figure 15. Excitation ($\lambda_{em}=525$ nm) and emission ($\lambda_{ex}=405$ nm) spectra for the new green Eu^{2+} phosphor

The XRD pattern could be unique within the known oxynitride phases, especially given the approximate composition of this material that had a relatively high oxygen concentration (Figure 16).

Figure 16. X-ray diffraction pattern for our new green Eu^{2+} phosphor in the $\text{BaO-Si}_3\text{N}_4\text{-SiO}_2$ system

Our initial samples had quantum efficiencies of $\sim 60\%$, which was very promising given that was no effort towards the optimization of this material. The decay time of this material is ~ 1.25 μs , so it will not suffer from any saturation issues in Lumination lamp designs. Also, the decay time is approximately constant from 485-605 nm (ranging from 1.23-1.28 μs or within experimental error), indicating that there is only one Eu^{2+} center in this material. Finally, the high temperature properties of this material show $<5\%$ quenching at $\sim 200^\circ\text{C}$, indicating that the ultimate efficiency of this phosphor could be quite high. As a reference point, this is already a significant improvement over our current green phosphors that have $>50\%$ quenching at 200°C (Figure 17).

Figure 17. Intensity vs. temperature for new green phosphor compared to a current green phosphor.

This has also been verified through decay time vs. T measurements where there is again virtually no sign of non-radiative transitions up to ~ 475 K ($\sim 200^\circ\text{C}$) (Figure 18), indicating the potential for higher efficiency phosphors with optimized synthesis.

Figure 18. Decay time (in μs) vs. temperature for new green phosphor.

Within this composition, we have investigated compositional modifications of the new phosphor material. By modifying some of the host cations, we are able to shift the emission maximum from ~ 525 nm to ~ 540 nm with some loss in the overall quantum efficiency of the material. However, since the emission maximum position of the green band is not critical, we did not investigate further any correlation between emission maximum and QE losses. In addition, a preliminary investigation of the effect of Eu^{2+} level on the room temperature and high temperature efficiency of this material showed evidence of concentration quenching. This is especially evident at high temperatures where the highly doped Eu^{2+} phosphor has stronger quenching (Figure 19).

Figure 19. Integrated intensity vs. temperature for new green phosphor with varying Eu²⁺ content

Since this new green phosphor meets the initial requirements to begin optimization, we began screening for the parameters that control the overall efficiency of this material. This includes both starting materials as well as firing and processing conditions. One critical part is the firing temperature for these materials. It appears that at relatively low firing temperatures, there are secondary phases that are formed which can be detrimental to the overall quantum efficiency. Since Eu²⁺ can go into these phases, this can lead to a “dead” absorption at 405 nm that does not give the luminescence of the desired phase. Continuing our optimization of this material, we have also found two initial parameters that appear to have an influence on the quantum efficiency of this material. It appears that additional firing steps with proper precursor selection (through the residual transition metal levels) can improve the quantum efficiency of this material (Table 7).

Table 7. Quantum efficiency vs. number of firings & Fe level in SiO₂ precursor for the new green phosphor

Fire	Fe level in SiO ₂	QE
1 st	60 ppm	60
2 nd	60 ppm	62
1 st	<10 ppm	65
2 nd	<10 ppm	74

We have also determined that the commercial Si₃N₄ precursor also has a significant amount of transition metal impurities (primarily Mo). However, it appears that any washing steps (acid/chelating agents) to attempt to remove this impurity do not have an effect on the quantum efficiency (Table 8).

Table 8. Quantum efficiency vs. number of firings washing steps for the Si₃N₄ precursor (using the low Fe precursor from Table 1) for the new green phosphor.

Fire	Precursor washing	QE/Abs
1 st	Unwashed	64/79
1 st	EDTA	64/76
1 st	HCl	64/75
3 rd	Unwashed	74/74
3 rd	EDTA	74/75
3 rd	HCl	74/75

Given these initial steps in optimizing this material and the relatively high performance, we initiated lamp testing at Lumination and also plaque reliability testing at GRC. Unfortunately, we observed some initial phosphor efficiency losses under LED irradiation (Figure 20).

Figure 20. Degradation of new green phosphor under LED irradiation

Similar screening experiments to improve the stability of this green phosphor show that the degradation in this material is more sensitive to phosphor synthesis versus orange phosphor#1. For example, it appears that lower QE phosphors have stronger damage versus higher QE phosphors. As part of the optimization of this material, we evaluated the root causes for this damage and using this information to further improve the synthesis of this material. The initial evaluation started at UGA by analyzing the position of the Eu^{2+} ground state within the host lattice bandgap using IR stimulated luminescence to determine if any deep traps are filled after excitation into the $\text{Eu}^{2+} 4f^7 \rightarrow 4f^6 5d^1$ luminescence band. Deep traps can act as centers that either absorb 405 nm light, stealing away intensity, or act as sinks for Eu^{2+} energy transfer, leading to a non-radiative transition. It appears that the lower quantum efficiency sample has a higher concentration of traps versus the high quantum efficiency sample, and that the onset for filling these traps at 80 K can overlap with 405 nm excitation of lower efficiency samples (Figure 21).

Figure 21. Excitation spectra for IR stimulated luminescence in various green phosphor samples.

However, it appears that there is still significant work to be done in the optimization of this material since these measurements also show that low concentrations of deeper traps are filled at room temperature (Figure 22).

Figure 22. IR stimulated emission intensity versus temperature for QE=87 green phosphor

These initial spectroscopic results are encouraging for the lumen maintenance of this material since it is possible to control and measure the relative trap density in this material through synthesis and compositional modifications. However, we have not resolved those reliability issues, and since we have discovered and/or developed alternate green phosphors, we have halted optimization work on this material. We have investigated some of the root causes for the poor phosphor reliability. Through decay time versus T measurements (Figure 23), UGA determined that the likely cause for the loss in efficiency is energy transfer to a center that is created after exposure to high fluxes of violet LED radiation. In addition, initial thermoluminescence measurements show that charge carriers (likely electrons after Eu^{2+} photoionization) are created after excitation by 405 nm LEDs (Figure 24), filling a deep trap that is not depopulated for $T < 250^\circ\text{C}$. With this data, we can create simple model of the degradation of this phosphor. The initial step is Eu^{2+} photoionization into the oxynitride conduction band, leading to a mobile electron. This mobile electron is then trapped by a host lattice defect, forming a color center that acts as a trap for excited Eu^{2+} ions, leading to a non-exponential decay (Figure 23).

Figure 23. Decay profiles ($\lambda_{\text{ex}}=405$ nm; $\lambda_{\text{em}}=520$ nm) for GP1 both before irradiation (labeled before) and after irradiation (versus temperature).

Figure 24. Thermoluminescence of GP1 after 405 nm LED excitation at room temperature. The various curves shown here represent different heating rates.

Screening and initial optimization of GP2

We began screening experiments towards the synthesis of this Eu^{2+} phosphor with $\lambda_{\text{max}} \sim 511$ nm (Figure 25). Our preliminary investigations explored the effect of firing temperature and starting materials on phosphor performance. This initial effort produced BG1 samples with room temperature quantum efficiencies of $\sim 85\%$ at 405 nm excitation. Further characterization indicated that these initial samples showed no loss (within measurement errors) after 100 hrs of testing for our plaque reliability protocol. However, subsequent samples had significantly lower QEs ($\sim 59\%$) without any apparent changes in the synthesis procedure. To optimize and understand the synthesis of the BG1 phosphor material, we ran designed experiments (DoEs) using firing temperature and fluxing reagents as variables. We observed that the thermal quenching was relatively robust to process changes provided the phosphor remained phase pure. This DoE successfully identified a two-stage thermal processing schedule capable of producing phase-pure material, and hence, reliable luminescent properties. These phase-pure materials exhibited good thermal-derating behavior (i.e., 13% derating at 150°C). Room-temperature quantum efficiency (i.e., typically 75%) displayed little variation with thermal processing.

Figure 25. Room temperature emission and excitation spectra for GP2.

A second DoE followed the first in order to explore variations with firing temperature and dwell times. We determined that an optimized preparation consisted of a two-stages (1000°C and 1150°C) in flowing 2% H_2/N_2 , each for a dwell time of 4 hours. Covering the crucibles was essential in preventing body color discolorations, which always indicated lower performance. The resulting optimized procedure routinely produced GP2 materials with 75-77% quantum

efficiencies and thermal deratings of 10–12% at 150°C. Occasional specimens exhibited higher quantum efficiencies (~84%) that approached the performance found in the original sample (i.e. 85%). Despite repeated attempts, however, we were unable to isolate the cause for this enhanced performance and generating GP2 materials with this level of quantum efficiency proved unpredictable.

However, given that our initial concern was regarding the synthesis repeatability of this phosphor, we focused on the modifying the phosphor emission color. From the results in Task 1 in Year 1 on this program, the usefulness of the GP2 phosphor material as a blend component would be significantly improved if the emission wavelength was shifted to >525 nm. Various experiments were conducted to influence the position of the $\text{Eu}^{2+} 4f^6 5d^1 \rightarrow 4f^7$ emission by modifying both the cation and anion compositions in this host (smaller cations to increase crystal fields; various anions to modify Eu^{2+} -ligand covalency). Unfortunately, the efforts to shift the luminescent wavelength towards yielded high concentrations of second phases that typically incorporated the elements that we wanted to incorporate into GP2 with shifts in the emission wavelength shifts. In addition, the presence of significant second phases also reduced both the room temperature quantum efficiency and thermal derating. Therefore, since the phosphor emission color is not optimal for high luminosity blends, we have made further work on this phosphor a lower priority. However, we have determined that this phosphor can be scaled up to a larger 40 g batch without any losses in room temperature QE, thermal derating, or plaque reliability. While LED testing is a secondary priority with this material, we will be noting if the addition of GP2 to any potential blends will give any benefits in the luminosity or CRI at incandescent/halogen color temperatures.

Screening and initial optimization of GP3

We began the study of this new phosphor based upon previous work studying the Ce^{3+} luminescence of a material that contains a “free” O^{2-} ion, defined as an O^{2-} anion that is only coordinated to larger RE^{3+} or alkaline earth cations. In hosts with “free” O^{2-} anions, the covalency of the Ce^{3+} -ligand bond is high, which can potentially lead to lower energy $\text{Ce}^{3+} 4f^1 \rightarrow 5d^1$ absorption transitions in the blue spectral region³. However, there is usually strong quenching of Ce^{3+} luminescence via photoionization⁴. If the quenching is by photoionization, increasing the host lattice bandgap should reduce this quenching. Therefore, we modified this composition to an oxyfluoride composition to increase the host bandgap and minimize photoionization-based quenching. In the original oxide material, the initial efficiencies were ~25% with >50% quenching at 150°C. However, the oxyfluoride modification of this phosphor led to materials with efficiencies of ~75% (Figure 26) with <15% quenching at 150°C, indicating potentially higher quantum efficiencies and validating our screening approach.

³ P. Dorenbos, Phys.Rev. B 64, 125117 (2001); P. Dorenbos, Phys. Rev. B 65, 235110 (2002).

⁴ G.J. Dirksen and G. Blasse, J. Alloys and Comp. **191**, 121 (1993).

Figure 26. Emission and excitation spectra of new Ce^{3+} blue-green phosphor.

However, while this material meets the requirements for the strong 405 nm excitation and high temperatures QE, the emission color is blue-green ($\lambda_{\text{max}} \sim 485$ nm) and needed to be shifted to lower energy for potential use in blends. Our initial modifications used solid solutions with other hosts with similar structures. These new compositions mainly modified the anion composition with appropriate charge compensation with the cations, and resulted in a significant red shift that made the phosphor more appropriate for white light blends (Figure 27).

Figure 27. Emission spectra of new Ce^{3+} green phosphors with a composition modified for green emission.

However, while the QE of this new phosphor was equivalent to the base composition, there was a significant reduction in the high temperature efficiency, where these greener phosphors had a loss of $\sim 33\%$ at 150°C versus $<15\%$ in the base composition. If the high temperature loss with greener emission was intrinsic, then this would effectively end work on this phosphor as with GP2. However, our work showed that modifying both the cation and anion compositions independently resulted in a significant redshift but without severe high temperature quenching (Figure 28). At this point, the efficiency of this material was $\sim 76\%$ with a loss of $\sim 15\%$ at 150°C .

Figure 28. Emission spectra of new Ce^{3+} phosphors in the GP3 family of compositions.

Since our initial experiments showed the potential for both green emission as well as high efficiencies at elevated temperatures, we began by looking for major factors that affect the phosphor QE at room and elevated temperatures. One strong factor was the Ce^{3+} level that indicated a strong concentration quenching in these materials, which shows that the majority of the quenching processes in these materials could be overcome by an optimized synthesis that removes defects causing non-radiative transitions after Ce^{3+} - Ce^{3+} energy migration. However, these experiments at lower Ce^{3+} levels again show that there are no fundamental trade-offs between emission color and efficiency (Table 9). In addition, in this experiment, the loss at 150°C for the 0.5% Ce^{3+} sample is $\sim 12\%$, further reinforcing the potential capabilities for green phosphors in this system.

Table 9. Summary of optical properties versus Ce^{3+} concentration for new green compositions

Sample	QE/Abs	(x,y)	λ_{max}
0.5% Ce	76/80	(0.351, 0.537)	532 nm
1% Ce	65/92	(0.384, 0.550)	541 nm
2% Ce	49/94	(0.413, 0.544)	551 nm
4% Ce	26/94	(0.452, 0.521)	565 nm

While spectrometer tests show significant promise for this material, our results on OP1 and GP1 have shown that we must account for phosphor reliability early in the development cycle. To start these screening experiments, we started LED stability testing of this phosphor using our in-house plaque testing capabilities at GRC with no apparent issues in the plaque stability testing (Figure 29). This sample was sent to Lumination for lamp testing, and initially showed no apparent lumen maintenance or color shift issues after ~ 500 hours of testing. Further testing will be detailed when discussing the results for Tasks 4 and 5.

Figure 29. Plaque reliability testing for radiation stability of Ce^{3+} doped phosphor in a blend with a standard red phosphor.

We also note that apart from radiation stability, another issue is the phosphor stability at high temperatures (85°C) and high humidity conditions (85% RH) (HTHH). Our initial blue-green compositions showed significant degradation ($>90\%$) when encapsulated in silicone under 100 hrs of HTHH conditions (Figure 14). However, in a fortuitous circumstance, it appears that the composition modifications that shift the phosphor emission towards the yellow-green also lead to a significant increase in moisture stability of the phosphor: there is less than 1% decrease in the intensity after 150 hours. (Figures 30 and 31)

Figure 30. Photographs (under 365 nm excitation) of various compositions within GP3 family when blended with a deep red standard phosphor after ~ 100 hrs exposure to HTHH environments. The sample on the right is deep red in color because the original green-yellow phosphor in the phosphor blend has degraded under HTHH.

Figure 31. Plaque reliability testing of Ce^{3+} doped GP3 blended with a standard deep red phosphor and encapsulated in silicone after extended exposure to 85% RH and 85°C .

Considering the flexibility for emission color, the initial phosphor efficiency, and the reliability screening for the GP3 phosphor, we down-selected this material for extensive composition and synthesis optimization.

Optimization of GP3 composition and synthesis

Our initial starting point was to evaluate various sources for the phosphor precursors, including commercial vendor and compound type (e.g., oxide, carbonate, nitrate, etc.). Measurements of QE and absorption from all samples were within experimental error suggesting the potential for a robust synthetic process to precursor variation. However, we noted that number of firings in this synthesis was reduced from 5 firings down to just two by replacing specific metal nitrates with metal oxides in the synthesis procedure. This makes synthesis significantly easier because of the reduction in the number firings as well as the elimination of metal nitrate sources that are hygroscopic. Using this procedure with less firing steps, we are able to more extensively map out the synthesis and composition parameters for this material.

Along with lower cerium levels, another synthesis variation was to map out the optimal limits for isovalent metal substitution and anion stoichiometry (Table 10). For high levels of substitution (i.e., > 50% for both isovalent metal and anion substitution), we observed luminescence from an undesirable second-phase that takes Ce^{3+} out of the desired phosphor, thereby reducing the phosphor absorption at 405 nm. We identified an optimal 40/40 level, and also re-confirmed the optimal Ce-doping (0.5%).

Table 10. Compositional DoE for isovalent metal levels and anion stoichiometry for 0.5% Ce^{3+} phosphors.

Metal	Anion	QE/Abs(405nm)	(x,y)	λ_{max}
40	40	84/80	(0.388, 0.54)	541 nm
40	60	77/75	(0.402, 0.538)	547 nm
50	50	70/62.5	(0.399, 0.534)	541 nm
60	40	75/63	(0.397, 0.535)	543 nm
60	60	69/55	(0.399, 0.53)	543 nm

Our next step with the 40/40 composition, we ran an initial design-of-experiments (DoE) on the flux levels and firing temperatures. As presented in Table 11, increases in the flux level (i.e., for a given firing temperature) indicated virtually no effect within measurement error. However, variation between the different firing temperatures yielded a slight bias towards a higher second firing temperature.

Table 11. Design of experiments results of flux level and firing temperature for the haloaluminosilicate phosphor. The influence of flux level was minimal although a slight bias towards a higher second firing temperature (i.e., 1200°C) is observed.

Flux level	2nd fire T	QE/A(405)	(x,y) at 405 nm
12.5%	1100	77/77	(0.375, 0.534)
25%	1100	78/76	(0.378, 0.534)
37.5%	1100	80/77	(0.386, 0.536)
12.5%	1150	79/80	(0.383, 0.537)

25%	1150	80/75	(0.386, 0.537)
37.5%	1150	80/73	(0.387, 0.537)
12.5%	1200	82/75	(0.383, 0.5365)
25%	1200	84/74	(0.386, 0.5365)
37.5%	1200	78/74	(0.388, 0.5365)

Fixing the flux level to 25%, we then screened for the firing temperatures and time. There was virtually no effect on the phosphor properties with different firing time, but there does appear to be some effect with the temperatures of the second firing (Table 12), yielded an optimal combination of 850°C and 1200°C. It is noted that these samples now have comparable quantum efficiency versus our blue-green phosphor sample, and therefore have an absolute quantum efficiency of 80-85% with a much higher efficiency at 150°C.

Table 12. Investigation of the initial and secondary firing temperatures. The combination of 850°C and 1200°C was determined to be optimal.

1st Firing	2nd Firing	QE/Abs(405)
750	1200	84/71
750	1250	64/74
850	1200	87.5/74

However, after these initial results for the GP3 phosphor, the quantum efficiency of GP3 drifted down by 5-8%. Our initial screening experiments to find the root cause for the lower efficiency included flow rate adjustments, hydrogen levels, batch sizes, and crucible geometries. Upon reviewing the synthesis procedure for our highest efficiency materials, we have observed that one specific furnace in our laboratory has given the highest efficiency materials. Our first task (in progress) is to check with multiple runs whether this furnace consistently gives higher efficiency materials. Unfortunately, this was not the case and there was a hidden factor that controlled the optimal synthesis of this phosphor. We next focused upon the gas flow rates and the hydrogen levels for >25 g batches of this new phosphor. In general, we have found that higher hydrogen levels and higher gas flow rates lead to higher quantum efficiencies for larger batches of our green phosphor. This might be the reason for the furnace differences since the furnace that gave higher QE samples generally had a higher gas flow rate. We also started to evaluate the potential root causes for the lower quantum efficiency. From our experiments, we find a correlation between the phosphor absorption in the visible spectral region and the phosphor quantum efficiency (Figure 32). We have evaluated whether this difference could be due to Ce^{4+} in the host that is not completely reduced. This was tested by annealing this phosphor in air at 700°C to oxidize it; while the quantum efficiency has dropped from ~85% to ~50%, there is no additional absorption band in the visible spectral region (Figure 33); in fact, it appears that there is slightly *less* absorption in the visible for the oxidized sample. The significant absorption in the deeper UV, however, could be assigned to Ce^{4+} , indicating that it does not play a role in the visible absorption. Further work is necessary to evaluate the cause of this absorption and try to eliminate it to maximize phosphor efficiency.

Figure 32. Diffuse reflectance of various batches of our new green phosphor

Figure 33. Diffuse reflectance of new green phosphor before and after oxidation.

Within GP3, we also analyzed the potential maximum efficiency at high temperatures. In order to study this, we synthesized very low doping levels ($<0.1\%$) and then analyzed the decay time as a function of temperature and excitation wavelength. The effects of excitation wavelength are critical here due to severe inhomogeneous broadening due to local compositional variations. Our initial analysis focused on the lower energy Ce^{3+} ions since our observations were that high dopant concentrations led to stronger high temperature quenching and a redshift in the emission. Consequently, we have excited this phosphor at ~ 520 nm, at the low energy tail of the excitation spectrum. It initially appears that quenching under 520 nm excitation is relatively small at high temperatures (Figure 34) with the decay time reaching $\sim 90\%$ of the room temperature value at ~ 425 K (150°C). Therefore, we believe that the quenching at higher dopant concentrations is due to energy migration to defects and not due to intrinsic luminescent processes. This also implies that improved synthesis processes can improve the room and high temperature efficiency of this material.

Figure 34. Decay time versus T for new green phosphor excited at very low energy excitation and emission

Apart from the slightly lower quantum efficiency at larger batch sizes, when using OP2 in combination with the GP3, we found that the color point of GP3 should be shifted towards the blue in order to maximize the lumen equivalent and the CRI of the tri-phosphor blend using blue/GP3/OP2 phosphors. In order to meet these color requirements, we went through an initial set of designed experiments for phosphor composition, varying alkaline earth cation levels and small cation levels with appropriate charge compensation. Through this, we found that for relatively small compositional changes, the quantum efficiency is equivalent within measurement errors, but there is a significant drop-off in phosphor efficiency for larger compositional changes (Table 13). This is not due to intrinsic quenching processes since the high temperature efficiency is retained for these compositions. These samples with larger compositional changes have significantly more glassy phase formation and are much more sintered versus the other samples in that set. This indicated that processing parameters could play an important role in bringing up the efficiency of this material. In order to address these issues, we screened for the temperature of the first and second firing of this material. We found that for blue-shifted phosphor compositions, a lower first firing temperature is necessary to reduce glassy phase formation in these materials. This glassy phase was initially attributed to a eutectic composition between a carbonate and fluoride precursor in the solid-state reaction. We presumed that if the carbonate precursor is fully decomposed, then the likelihood for this eutectic formation is reduced, thereby preventing a low temperature liquid and glassy phase formation. Further evidence on the effect of potential eutectic composition formation on phosphor efficiency and glassy phase formation are given later in this section.

Table 13. Composition modifications with color and efficiency for new green phosphors

Levels	x	y	QE	Abs
40/40	0.391	0.545	>85	78
30/30	0.372	0.547	84	86
25/25	0.346	0.538	69	85

We also screened alternate fluxing systems (beyond the typical flux given in Table 11) in this system to see if different fluxes can affect the quantum efficiency and absorption of these new phosphors. We screened various chlorides and borates that are known to be effective fluxing systems in other phosphors. We observed that the addition of these fluxes lead to severe sintering of the phosphor cakes, making these cakes unprocessable at high flux levels. At lower flux levels, the phosphor cakes can be processed, but there were no observable improvements in the phosphor efficiency. We have also made these materials using elemental oxides versus carbonate precursors to eliminate one issue in the decomposition of carbonate precursors during solid-state reaction. In these initial experiments, we did not see any statistically significant differences between these samples.

Since GP3 requires two firing steps, we also screened for the blending/grinding of these samples after the first firing. This can be an issue since these materials are often severely sintered after the first firing step and require extensive break-up before the second firing. We did not see any differences in the phosphor quantum efficiency (QE), but there appears to be higher absorptions for larger batch samples due to a shift in the particle size distribution (Table 14).

Table 14. Screening DoE for blending, sieves, and batch size for GP3 phosphor.

Blending sieve	Batch size	Particle size	QE/abs
60 mesh	30 g	12/39/72	85/83
60 mesh + reblend	30 g	12/36/72	61/83
140 mesh	30 g	14/38/66	82/83
270 mesh	30 g	Not tested	Glassy
60 mesh	10 g	8/31/61	83/80
60 mesh + reblend	10 g	8/30/57	82/80
140 mesh	10 g	9/33/61	83/80
270 mesh	10 g	8/31/63	85/80

Since there was little to no rational correlation for the process parameters in these experiments, we went through some of the precursor reactions in order to understand the process for phosphor formation to avoid potential side phase/glass formation and determine potential routes for further efficiency improvements. In this manner, we have separated the various precursors based upon the x-ray diffraction (XRD) results after the initial low temperature fire of this material. By separating the reactions, all of the powder handling in these experiments becomes straightforward and none of the powders are severely sintered in 5-10 g batches. However, even when separating out all reactions, we observed some initial scale-up issues for GP3. There is some degree of process variability in that ~20% of the samples have significant glassy phase formation that makes it impossible to process this material for use in lamps (Figure 35). As noted above, we initially believed that the cause for this additional glassy phase is due to incomplete decomposition of some of the carbonate precursors that are used in this synthesis.

Figure 35. New yellow-green phosphor cake showing significant secondary glassy phases.

The role of carbonate decomposition was verified through additional small-scale experiments. In the synthesis of this phosphor, there is an initial low temperature firing step followed by re-blending with a flux and a higher temperature firing step. The conditions within the first fire are critical to determining the final properties of the phosphor. Specifically, if the alkaline-earth carbonates that are used in this process are not completely decomposed, then there is a significant amount of “glassy” phase in the final phosphor cakes. This was determined by taking the same initial blend of starting precursors and firing in closed and open crucibles (Figure 36). The worst result was in a closed crucible that was placed inside of a closed charcoal crucible (denoted as CCP in Figure 36) that will slow the decomposition of alkaline earth carbonates due to the CO/CO₂ atmosphere in a closed crucible containing charcoal. As noted numerous times in this section, the “glassy” phase makes processing of the phosphor cakes difficult as well as reduces the overall quantum efficiency of the phosphor in plaque measurements.

Figure 36. Phosphor cakes versus different conditions in the 1st firing conditions for our new yellow-green phosphor.

Identifying the root cause for synthesis issues has also led to improvements in the plaque efficiency of larger batch samples (>50 g). Using an open crucible in the 1st fire of this phosphor, has led to ~4-5% improvements in the plaque quantum efficiency of this material. This key point within the synthesis of a specific GP3 phosphor can be applied to all compositions

within this family of materials. In addition, we used this fundamental process knowledge described to go back and determine if the optimal compositions from our previous synthesis process still apply with this new synthesis process. In our experiments for Ce^{3+} concentration, we previously determined that room temperature concentration quenching began at $\sim 0.5\%$ Ce^{3+} (Table 9). However, in our new synthesis process, we find that this concentration limit is synthesis dependent, and that the phosphor quantum efficiency appears to be constant up to $\sim 1\%$ Ce^{3+} concentration (Table 15). This is an important result since the ability to have higher Ce^{3+} concentrations without severe quenching can enable further improvements in lamp efficacy by reducing scattering losses. There is additional thermal quenching of this phosphor at higher Ce^{3+} concentrations, but additional work will be necessary to address the relative thermal and scattering losses when incorporating this phosphor into LED packages and lamps at GE Lumination. We also re-screened additional yellow compositional modifications of this phosphor in our new synthesis method (Table 15). However, we see similar solid solubility limits (and second phase formation) for this material when compared to our previous synthesis, indicating that the compositional limits that were determined previously are likely from thermodynamic limitations and not due to kinetics or side reactions in the synthesis process.

Table 15. Compositional modifications of our new yellow-green phosphor (A/B are cation modifications, Ce is the relative Ce concentration) using the new synthesis that accounts for carbonate decomposition and eutectic formation.

A/B/Ce	QE/Abs	HT (150°C)	(x,y) at 405 nm	(x,y) at 450 nm
40/40/0.5	89/73	88	(0.390, 0.540)	(0.413, 0.550)
45/45/0.5	89/72	87	(0.397, 0.539)	(0.423, 0.543)
50/50/0.5	90/69	85	(0.408, 0.539)	(0.430, 0.540)
40/40/0.75	88/82	82	(0.404, 0.544)	(0.423, 0.543)
40/40/1.0	89/87	78	(0.413, 0.543)	(0.429, 0.541)

Finally, we have also worked on the processing of these materials for optimization in lamp testing in our initial synthesis process (where there might have been additional glassy phases that compromised phosphor QE). In our initial samples, our colleagues at GE Lumination commented that the phosphor particle size was generally large, which led to clogs in the phosphor/silicone dispensing system. In addition, some of the larger particles are visible in the coating, detracting from the aesthetic appearance of the lamps as well as leading to color separation in lamps. We therefore investigated methods to control the particle size distribution of our new green phosphor while maximizing the efficiency and the absorption of this material. Our initial experiments focused on wet-milling this phosphor in isopropanol (IPA) until the median particle size (d_{50}) was $<20\ \mu\text{m}$. However, this milling process created a significant number of fine particles that strongly scatter incident light and lower the sample absorption (Table 16). These fine particles were removed by settling larger particles in IPA and decanting smaller particles in the supernatant. This leads to a “classified” phosphor sample. This procedure does lead to some materials loss that could be an issue in the future scale-up of this material, but the optical properties of the classified phosphor sample show improved absorption with no losses in QE within measurement errors. This process has also been adapted to the improved phosphors with similar results. Any lamp tests use this classified phosphor to see if there are any changes in the lamp performance/aesthetics and reliability. We do not expect any changes in the room temperature reliability, but a smaller particle size could affect the 85C/85%RH reliability.

Table 16. Optical properties versus processing parameters for new green phosphors.

Particle size distribution $d_{10}/d_{50}/d_{90}$ (μm)	Processing	QE*ABS
2.7/11.2/22.8	IPA wet mill	85/64
3.9/12.0/23.2	Fines removed	85/68
3.3/12.0/23.4	IPA wet mill	81/68
5.6/13.3/24.9	Fines removed	79/74

Screening of other new materials

The examples detailed in this section are representative of the vast majority of our new materials made in this program. In this regard, we based our initial screening experiments on two main strategies:

1. Doping of known host lattices with either Ce^{3+} or Eu^{2+} and then assessing the excitation, emission, and high temperature quenching of these materials. In this regard, we use the basic design rules for phosphor synthesis developed in Task 1 as a guideline for prioritizing compositions for screening. Examples of resources that can be used for new hosts are the ICSD and JCPDS databases for structural and x-ray data, respectively as well as mineralogical databases.
2. High throughput screening (or combinatorial) methods to attempt to accelerate the discovery of new phosphor materials. To do this, we take slurries of powder compounds, dispense given volumes of them in alumina crucibles, and fire these mixtures in different atmospheres. This allows us to go through and screen within large areas of phase space in single experiments. Our design rules aid from Task 1 aid us by limiting the total design space for compositional screening.

Within these (or any) screening experiments, there is always the concern of observing luminescence from known phosphors that are present as minor phases within our synthesis. Within these experiments, we have found materials that have given emission and excitation spectra that are distinctly different versus known phosphor compositions. However, all of these materials (with the exception of the OP1-OP3 and GP1-GP3 phosphors described in detail above) have typically failed our requirements for high temperature efficiency. However, while quantifying the reasons behind their low efficiency is a part of this program, we have focused more towards optimizing the down-selected phosphor compositions with greater promise. Future work could involve additional characterization of these materials in order to understand the roles that composition and synthesis play on the efficiency of LED phosphors.

Within this framework of new material screening, some examples for the different compounds that have been screened include:

Silicate-based systems:

A series of compositions were screened within alkali-alkaline earth- SiO_2 ternary system using Eu_2O_3 at 1 mole % with respect to the entire mixture. The samples were fired at temperatures ranging from 750 to 1100C in 1% H_2/N_2 . The majority of the obtained samples had blue-green luminescence with the $\lambda_{\text{max}} = 505$ nm upon excitation at 405 nm (Figure 37).

Figure 37. Representative emission spectra ($\lambda_{\text{ex}}=405$ nm) for alkali earth-alkaline earth-SiO₂ materials

However, analysis of the excitation, emission and x-ray diffraction pattern showed that the materials made in these experiments were typical alkaline earth silicates with no new phase formation. Therefore, this phase space was also expanded to include halide incorporation into these materials. In many of these systems, the additional halide sources acted as a flux for the formation of the alkaline earth silicates, thereby leading to strongly sintered cakes of typical alkaline earth silicate phosphors. In a couple of cases, we did find alternate phases apart from typical alkaline earth silicates (Figure 38).

Figure 38. Emission spectra ($\lambda_{\text{ex}}=405$ nm) of materials within alkali halide-alkaline earth-SiO₂ phase systems

However, while the emission and excitation of this material was potentially promising, the losses at high temperature were exceedingly high (>50% at 150°C) even at relatively low Eu²⁺ concentrations to consider moving forward with further work on this material.

Nitride-based systems:

Apart from the new green composition described above, we have used high throughput screening to investigate other nitride and oxynitride spaces. This has given a new yellow-orange material that can be excited by 405 nm radiation (Figure 39).

Figure 39. Potential yellow-orange phosphor discovered via high throughput screening.

The excitation, emission, and x-ray diffraction pattern of this material appear to be unique compared to prior reports within the literature. However, at this time, we have observed severe thermal quenching of the Eu^{2+} luminescence ($>30\%$ at 100°C) that will likely prevent any potential application of this material. With these materials, we also initially evaluated the synthesis process (firing conditions, starting materials, etc.), but there was no significant reduction in the quenching at high temperatures.

Within the nitride and oxynitride hosts, we have also initiated screening experiments on alternate nitride compositions that do not contain Si^{4+} , unlike virtually all systems reported in the open literature. There are nitride compositions with P^{5+} as well, so we have screened materials within these systems. In certain compositions, we observe characteristic Eu^{2+} luminescence (Figure 40) with absorption at 405 nm.

Figure 40. Eu^{2+} luminescence in a phosphorus nitride based host

However, the initial quantum efficiency of these materials are low, and they show strong quenching at 300 K versus 10 K ($>70\%$). Currently, it also appears to be quite difficult to synthesize a wide variety of materials in this system using standard solid-state synthesis due to the limited reactivity and high volatility of the P_3N_5 precursor. Therefore, new synthesis methods need to be developed in order to determine if other P^{5+} compositions can be used as LED phosphors.

Borate-based systems:

While borate based systems have been studied to some extent for Eu^{2+} -based phosphors⁵, there are fewer reports on Ce^{3+} luminescence within the extensive set of borate hosts. Our initial investigations within these systems have shown that many of these materials in these phase spaces generally have a deeper blue Ce^{3+} emission with little to no excitation at 405 nm (Figure 41).

Figure 41. Representative excitation and emission spectra for alkali earth-alkaline earth- B_2O_3 phases

Modifying these compositions does not significantly move the excitation spectrum towards 405 nm, making these materials less useful for LED-based SSL. We have also found other alkaline-earth borate systems that have Ce^{3+} emission at ~ 470 - 480 nm, and have found that it is possible to shift the emission of these phosphors to ~ 520 nm, making it potentially useful for a violet LED phosphor (Figure 42). The initial efficiency is $\sim 70\%$, which is promising for a sample made the first time. However, our initial measurements also show that the quenching at 150°C is $\sim 30\%$, significantly higher than our current yellow-green phosphor (~ 12 - 14% loss at 150°C). However, it appears that the high temperature quenching of this phosphor is retained even for very low Ce^{3+} concentrations (unlike GP3). Consequently, we have submitted a patent application covering these compositions but have not pursued them further within this program.

Figure 42. Emission and excitation spectra for new Ce^{3+} alkaline earth borate

Phosphate halides:

⁵ Diaz and Keszler, Mater. Res. Bull. **31**, 147 (1996).

We found a potential deeper red phosphor with <15% quenching at 150°C in Eu^{2+} -doped phosphate halides with alkaline and alkali earth metals (Figure 43). Currently, the emission of this phosphor is too deep in the red, so the lumen equivalent of this phosphor is low. In addition, from initial washing experiments in water, it also appears that this phosphor is moisture stable. Therefore, our initial task is to determine how to shift the emission of this phosphor towards shorter wavelengths. In these hosts, there are possible substitutions for monovalent and divalent cations as well as for the anions in this host. We will be investigating these substitutions for the color, excitation and high temperature quenching of any new phosphors within this system. The eventual goal would be to have a deep red phosphor with an emission at ~620-640 nm that would supplement our current green and orange phosphors to make higher CRI light sources.

Figure 43. Emission spectra versus temperature for potential new phosphor in the phosphate halide system ($\lambda_{\text{ex}}=405$ nm).

We improved upon the synthesis of this phosphor by slowing the furnace ramp rates during the cooling process. This has yielded a phosphor with an initial QE of 50%. However, in initial plaque reliability studies, we have observed some degradation of this material (Figure 44). Our improvements in the synthesis of this material have also reduce the degradation of this material, indicating that this phosphor's degradation is at least partially controlled by synthesis conditions. However, this is a potential issue when that must be tested at all points for any modifications of this material.

Figure 44. Emission spectra versus irradiation time for blends of our potential new phosphor ($\lambda_{\text{ex}}=405$ nm) and a GE Lumination standard blue-green phosphor.

Other materials:

Apart from nitride and oxynitride hosts, most typical Eu^{2+} phosphors are based upon alkaline earth phosphates, aluminates, and silicate whose host lattices consist of ions with noble gas configuration. In general, hosts that have high concentrations of ions with d^0 or d^{10} configurations do not show any Eu^{2+} luminescence due to photoionization processes. Quenching via photoionization can also be thought of as a virtual reduction-oxidation process where Eu^{2+} ions are oxidized and the d^0/d^{10} ions are reduced. Consequently, choosing host lattices with d^0/d^{10} ions that are more difficult to reduce (i.e. have a lower ionization potential for the reduced ion) could offer another route for discovering new Eu^{2+} compounds. We initially investigated alkaline earth tantalates since Ta^{5+} is known to be extremely difficult to reduce to lower valence states. We observe characteristic Eu^{2+} luminescence in some alkaline earth tantalates; this has not been reported in the open literature to the best of our knowledge (Figure 45).

Figure 45. Emission and excitation of alkaline earth tantalates doped with Eu^{2+}

The examples detailed in this section are representative of the vast majority of the materials made in this program. As noted above, these materials do not currently meet the requirements for high efficiency either at room or at elevated temperatures, making them unsuitable for use in high efficiency LED lighting. However, these different materials show that routes apart from the typical nitride, phosphate, aluminate, and silicate hosts can lead to $\text{Ce}^{3+}/\text{Eu}^{2+}$ absorption of blue or violet LED excitation with green, orange, or red emission. These results further demonstrate that there are still many compositional spaces that can be investigated for new $\text{Ce}^{3+}/\text{Eu}^{2+}$ LED phosphors.

Milestones for Task 2- Develop new phosphor compositions

One phosphor composition for downselection meeting spectral requirements (4/2007)

We developed a new green oxynitride phosphor material (GP1) that met the spectral requirements for green phosphors and had an initial efficiencies of ~75% compared to typical Lumination green phosphors. There is strong absorption at 405 nm and <5% quenching at 150°C. Therefore, this material was our first composition for downselection.

Two compositions (overall) selected for optimization based upon spectral requirements & spectroscopic evaluation (9/2007)

We developed three potential yellow-orange compositions that could meet the spectral requirements detailed above. We initially selected one phosphor composition due to its improved high temperature efficiency. However, there are some issues in the reliability of this

phosphor. The other yellow-orange phosphors have significantly better reliability, so our initial yellow-orange phosphor might require significantly more time and effort in optimization versus compositions #2 and #3. However, we believe that we currently have multiple yellow-orange phosphor compositions that can be optimized and meet the requirements for high efficiency LED lighting.

Downselection of red and green phosphor compositions that meet spectral requirements from Task 1 and pass initial spectroscopy tests at UGA for optimization downselection (no photoionization, fast decay time, thermal quenching) (9/2008)

At the end of Year 1 of this program, we had identified one new green phosphor (GP1) and three orange phosphors (denoted as OP1, OP2, and OP3) that could meet spectral requirements as well as having reduced thermal quenching compared to the current phosphors in the Lumination Vio product. In our initial LED testing, we observed significant phosphor reliability issues with GP1 and OP1, halting significant optimization work on these materials. However, the other yellow-orange phosphors (OP2 and OP3) have shown better initial reliability with no losses out to 5000 hours of lamp testing, so our downselection and optimization tasks (Task#3) for orange phosphors have focused on these two compositions.

The reliability issues for GP1 focused the Task#2 work in Year 2 towards green and green-yellow phosphor compositions. To meet these spectral requirements, we first identified a Eu^{2+} -doped halosilicate composition (GP2) within older GE intellectual property whose emission maximum was at ~512 nm with strong excitation from 390-450 nm. Initial samples showed quantum efficiencies of ~65% with thermal quenching of <15% at 150°C, meeting the initial screening requirements. We worked on trying to shift the Eu^{2+} emission maximum to longer wavelengths to improve the blend properties of this material. However, this work was generally unsuccessful so this material was not optimized further.

To meet the green spectral requirements, our screening experiments also gave us a new Ce^{3+} haloaluminosilicate phosphor (GP3). We were able to tune the emission color from the blue-green to the green-yellow through compositional adjustments. Our initial focus was to map out the appropriate compositional space to determine if there are any trade-offs between room temperature quantum efficiency, color, and thermal quenching, and there did not appear to be any significant trade-offs. All of these initial materials had reasonable initial quantum efficiency (~65%), high temperature efficiency (<15% loss at 150°C), and passed initial reliability screening tests.

Milestones for Task 3 - Synthesis optimization of new phosphor compositions

Improvement in quantum efficiency for one phosphor compositions by >10% (4/2008)

Through modifications in firing conditions and also starting precursors, we have already improved the quantum efficiency of the GP1 composition by >10%. In addition for our OP1, OP2, and OP3 yellow-orange phosphors, we have also determined some key variables, such as the crucible, that play a role in the phase purity and phosphor efficiency.

Optimization of at least one downselected phosphor compositions from Task 2 with >85% QE (9/2008)

For the OP2 phosphor composition, we have run designed experiments (DoEs) covering the composition (activator ion levels, non-stoichiometry), starting materials, and firing conditions (number of fires, temperature, time, atmosphere, crucible composition, flow rate) for 5-10 g batches of this material. Using the results from these DoEs, we have improved the QE of this material to ~82-85%, meeting the milestone of a >85% QE. In addition, we have also synthesized 50 g of phosphor per furnace run of this material without any losses in the efficiency, indicating no initial scale-up issues and allowing for blend development and lamp testing.

Improvement in QE of red and green downselected phosphor compositions from Task 2 by >10% (4/2009)

Optimization of at least one additional downselected phosphor compositions from Task 2 with >85% QE (9/2009)

For the GP3 phosphor composition, the largest initial limitation during phosphor optimization was relatively severe Ce^{3+} concentration quenching. Higher Ce^{3+} concentrations shift the emission towards the yellow spectral region at the cost of high temperature efficiency. Once this key parameter was identified, we have fixed the Ce^{3+} concentration within this sample and started our designed experiments around the processing of this material. Our initial improvement was to reduce the number of firing steps from five firings to two firings, which reduced both the sample variability and also improve the quantum efficiency from ~65% to ~77%. Further optimization of this material involving the fluxing and materials precursors has improved the efficiency of this material to >85%, again leading to an absolute QE>85% under 405 nm excitation. This high efficiency is maintained throughout the entire spectral range for this phosphor. We have developed a 50 g scale synthesis for one yellow and green phosphor composition to enable blend development and lamp testing. In addition, we determined some of the key processing parameters that can limit both phosphor yield and efficiency for larger scale synthesis. This information is necessary to ensure a smooth transfer of this synthesis procedure to GE Lumination.

Summary and comparison to current Vio™ phosphors

The phosphor development and optimization in this program screened through numerous compositions, and we down-selected the OP2 and GP3 compositions that had the potential to meet the various requirements for high efficacy lamps. After the completing optimization of OP2 and GP3, the properties of these phosphors show significant improvements at room and high temperatures versus the current Vio™ phosphor (Table 17). These results give us confidence in moving forward with lamp testing.

Table 17. OP2 and GP3 performance in laboratory measurements versus current Vio™ phosphors

Phosphor	QE	Derating at 150°C
OP2	85	18%
Current Vio™ yellow	75	40%
GP3	87-90	13%
Current Vio™ green	85	50%

Task 3- *Synthesis optimization of new phosphor compositions*

Task 4- *Incorporate phosphor materials into polymeric binders and composite processing*

Task 5- *Build and evaluate violet LED-based lamps*

Incorporation of new phosphors into silicones

The OP1, OP2, OP3, and GP1 phosphors do not react with moisture, water, or dilute acids; therefore, it was thought that there should be minimal reactions with the silicone binders that GE Lumination uses in lamp making. In our tests, the phosphor decay time did not change when phosphor powders were incorporated into typical GE Lumination silicones, and there were no additional induced absorption bands after incorporating these phosphors into the silicones. There were some concerns about potential photo-induced reactions between the phosphor and silicone that led to the reliability issues for the OP1 and GP1 phosphor compositions. However, our plaque reliability testing on the OP1 and GP1 powders without any silicone binders (Figures 9, 11, and 20) indicated the phosphor degradation is independent of any silicone binder. In contrast, we have shown that the GP3 phosphor does have some moisture sensitivity under high temperature/high humidity conditions (Figure 30). However, when incorporating this phosphor into GE Lumination silicones, the decay time of GP3 does not change and no additional absorption bands are present in the phosphor/silicone dispersions. Given the absence of reactions between the GE Lumination silicones and the phosphors developed in this program, we did not spend significant effort on developing new methods to incorporate these phosphor powders into silicones. This effort was re-focused on additional phosphor development (**Tasks 2/3**).

Initial LED lamp testing for reliability screening

Initial LED lamp testing was used to downselect phosphors for composition/synthesis optimization as noted in the detailed discussion for **Tasks 2/3**. Apart from setting a baseline value for phosphor reliability, these lamp tests are not necessarily relevant for assessing the efficacy, CCT range, and CRI range of lamps that use these phosphors. Therefore, we will only summarize the results of our initial lamp tests with respect to the phosphor reliability. For the OP1 and GP1 phosphors, we observed very severe lumen maintenance issues with >10% phosphor efficiency losses for $t < 100$ hours in VioTM prototype packages. We also tested the reliability of the OP1 phosphor in blue LED packages in blends with typical yellow phosphors; the phosphor/silicone dispersion was directly deposited on the LED chip. While the degradation was reduced in these blue LED packages, there is still apparent degradation of OP1 at relatively short times (Figure 46). These results further led the team to completely stop optimization work on OP1 and GP1.

Figure 46. Testing of phosphor blends with OP1 in 460 nm LED packages

In contrast to OP1, initial samples of the OP2 and OP3 compositions showed no sign of color shift or lumen depreciation after >10,000 hours in VioTM prototype packages. Similarly, we also tested initial samples of the GP3 phosphor in VioTM-like prototypes using both 450 nm and 405 nm LEDs. In both cases, we have not observed any statistically significant phosphor color shift or lumen depreciation in these test lamps to >10,000 hours in room temperature and high temperature, high humidity (HTHH) testing. One point to note is that the phosphor optimization tasks did not wait for long-term reliability tests to be completed. However, in our experience, any samples that fails our plaque reliability tests at t~100 hours fails LED reliability testing, and samples that pass the same plaque reliability tests have had no issues in LED reliability testing.

Lamp testing using (more) optimized phosphors

Given the optimization work in **Task 3**, we tested the performance of the OP2 and GP3 phosphors in a variety of blends using both 405 nm and 450 nm LED packages. As a starting point, the 405 nm phosphor blends used a combination of OP2, GP3, and a Eu²⁺-doped halophosphate (blue) that is used in Hg fluorescent lighting. The 450 nm phosphor blends used the GP3 phosphor and a deep red phosphor independently developed by GE Lumination. We separate the discussion of 405 nm and 450 nm lamp results for comparisons in this report. However, we realize that future customers primarily care about overall lamp performance, regardless of LED wavelength.

Lamp performance and iterations using 405 nm LEDs

One of our initial assumptions was that a similar GP3 composition could be used for both 405 and 450 nm LEDs. However, the initial lamp tests with 405 nm LEDs showed that for warm white color temperature (~2650 K) (Figure 47), the CRI of these devices was <80, which is less than the goals of this program. Again, this blend helps to assess phosphor reliability, and devices using these phosphors have passed >8,000 hours without any lumen depreciation (<2%) or lamp color shift (within 3 MacAdam ellipses). One way to improve the CRI of these devices was to blueshift the Ce³⁺ emission band for the GP3 phosphor band (Figure 47), which can be accommodated through the compositional flexibility of this phosphor (Figures 27 and 28; Tables 10, 13, and 15).

Figure 47. Spectrum of lamp using blue GE Lumination phosphor in combination with new green and orange phosphors developed in this program.

The initial color target for lamp tests with OP2 and the 405 nm modification of GP3 was CCT<3200K, CRI~80 using 405 nm based LEDs. With some adjustment of the blend composition, we were able to come close to those color targets. Within blend development, there was extensive work toward reaching color points that were near the blackbody locus. In spite of using the Ce^{3+} - Eu^{2+} combination that reduced the Eu^{2+} absorption in the visible, there still was significant phosphor re-absorption by the OP2 and GP3 phosphor. Also, since the blue phosphor was designed for fluorescent lamps (where phosphor cost is a critical parameter), it generally had a smaller particle size and Eu^{2+} concentrations. All of these factors make the weight percentage of the blue phosphor surprisingly high in these blends (>35 wt%) in spite of the relatively small spectral component. While these limitations for the blue phosphor are one avenue for overall improvement, these issues are also present for typical VioTM lamps, so we felt that it is reasonable to compare the performance of blue/OP2/GP3 blends with those used in current VioTM lamps with a similar color point (Table 18)

Table 18. Lamp performance of new phosphor blends in comparison to current VioTM lamps

Blend	Lumens	(x,y)	CCT/CRI
Test blend	167	(0.425, 0.408)	3245/82
Current Vio TM	137	(0.420, 0.405)	3324/85

In a variety of blends using GP3 and OP2, we have seen a similar performance versus current VioTM lamps with a 7-15% improvement over the current VioTM phosphor blend (for instantaneous measurements) at similar color temperatures and CRIs. The extent of this improvement in an “instantaneous” measurement (where the package/phosphor does not heat up during the measurement) is somewhat larger than our expected improvements of ~10% in instantaneous measurements. We have narrowed the root cause of the additional improvement to either reduced scattering losses within the package since the phosphor coating to reach the required color point is slightly thinner versus the current VioTM blend or saturation effects for the deep red phosphor within the VioTM blend. When making a comparison to a steady-state measurement, we would expect even more improvement relative to a typical VioTM package due to these phosphors’ improved high temperature efficiency (Table 17). We also expected larger improvements in the steady-state performance for 6-chip VioTM packages versus 3-chip VioTM packages since the phosphor layer will be heated further due to the ~2x higher LED flux on the

phosphor. This is seen in our experiments comparing our new phosphor blends and the current Vio™ blends (Figure 48). These experiments use different LED light engines (unlike our experiments for instantaneous measurements), so differences in the LED chip efficiency are not separated out in this data. However, it is clear that 3-chip and 6-chip Vio™ packages using our new phosphor blend have significantly less quenching at steady state versus the current Vio™ blend. For the 3-chip package at 350 mA drive current, this would add another ~10% improvement in efficacy (above the instantaneous measurement) for the new phosphor blend. The gains for the 6-chip package are even larger, and would be of the order of ~40%, since the phosphor temperature in this package is $>135^{\circ}\text{C}$.

Figure 48. Lumens versus time for new phosphor blends in 3-chip and 6-chip Vio packages attached to finned aluminum heat sinks showing thermal losses as the package heats up to steady state.

We have also started reliability testing on these higher efficacy lamps. As noted above, the initial tests using our GP3 and OP2 (CCT=2650K, CRI~75) have passed >7000 hours of testing with no significant sign of lumen depreciation or color shift beyond measurement variation (Table 19). Under HTHH testing, these devices show a shift in the V_f , which is generally independent of the phosphor and point to potential LED chip issues. Under room temperature testing, there is no sign of this V_f shift. For our newer lamp tests that use a modified GP3, there appears to be a distinct shift in the y color coordinate in the HTHH tests versus the room temperature tests (Tables 20 and 21). This could be an indication of degradation of this phosphor at HTHH conditions, but further work is necessary to determine this. In contrast, at room temperature, similar lamps have passed ~3000 hours of testing under room temperature

operation conditions without any sign of lumen depreciation or color shift. Since this is a potential limitation in using these new phosphors, we will also discuss some methods to protect phosphors from moisture sensitivity that we have developed/tested in this program.

Table 19. Lumen output and color coordinates for lamps (average of 5 lamps in HTHH testing) using initial samples of GP3 and OP2 with lamp operation time.

Hours	Lumens	x	y
0	149	0.469	0.415
1192	161	0.467	0.415
4321	169	0.467	0.415
7320	160	0.467	0.415

Table 20. Color coordinates versus lamp operation time for lamps (average of 5 lamps) in room temperature lamp testing using modified GP3 and OP2 phosphors

Hours	Lumens	x	y
0	158.4	0.4564	0.4300
169	157.6	0.4539	0.4296
382	161.0	0.4549	0.4297
546	163.1	0.4550	0.4301
710	164.7	0.4557	0.4303
1635	163.6	0.4561	0.4306
2372	163.0	0.4556	0.4309

Table 21. Color coordinates versus lamp operation time for lamps (average of 5 lamps) in HTHH testing using modified GP3 and OP2 phosphors

Hours	Lumens	x	y
0	159	0.4508	0.4270
169	158	0.4497	0.4263
382	166	0.4497	0.4258
546	166	0.4498	0.4257
710	167	0.4500	0.4257
1635	167	0.4504	0.4247
2372	167	0.4502	0.4233

At this time, the maximum measured efficacy (nominal 350 mA drive current, instantaneous measurement) for our OP2/GP3/blue phosphor blends for CCT=3200-3500K and CRI~82-85 is ~55 lm/W in a 3- chip Vio™ prototype using LEDs with at 40% wall-plug efficiency (WPE). Scaling this efficacy to a 50% WPE LED would then give an efficacy of ~69 lm/W, which is significantly below our program deliverables. We believe that while our new phosphors have significantly higher efficiencies, there are still large package losses within the Vio™ package that need to be addressed to fully optimize light output. Some potential routes to reduce these losses will be discussed in the **Future work** section.

Lamp performance and iterations using 450 nm LEDs

The original intent for this program was to develop phosphors for violet LED-based systems. However, given the progress at GE Lumination in their internal phosphor development program toward the discovery and optimization of red line emitting Mn^{4+} phosphors (Figure 49), denoted as RP, as well as the ability for specific compositions of GP3 to be used as a 450 nm phosphor (Figure 50), we felt that this it would be useful to test the performance of blends using these phosphors. In addition, using 450 nm LEDs would reduce Stokes losses by ~10% while still retaining high phosphor efficiencies. Initial blend calculations also showed that it could be possible to have luminosities ~332 lm/W-rad at CCT<3000 K and CRI~88 (Figure 51). This meets the 330 lm/W-rad at CRI~80 milestone for phosphor luminosity at much higher CRIs and with $R_9 > 60$.

Figure 49. Excitation ($\lambda_{em}=633$ nm) and emission spectra ($\lambda_{ex}=450$ nm) for a RP composition. The sharp lines from 440-500 nm in the excitation spectrum are artifacts from the Xe lamp source.

Figure 50. Room temperature excitation ($\lambda_{em}=550$ nm) and emission spectra ($\lambda_{ex}=405$ nm and $\lambda_{ex}=450$ nm) for one GP3 composition. The sharp lines from 440-500 nm in the excitation spectrum are artifacts from the Xe lamp source.

Figure 51. Calculated blend using GP3, RP, and a violet-blue LED chip.

While blend calculations are useful to determine the potential utility of new phosphors in LED packages, there are no substitutes for lamp testing. In our initial lamp tests, we tested blends of GP3 and RP with various blue LEDs to determine an optimal point for the blue LED wavelength (Table 22). It is clear that while RP can be used for various blue LEDs (Figure 49), GP3 is generally limited to blue LEDs with a maximum of <450 nm (Figure 50). This is evident in our lamp tests for the GP3/RP blends in three LED packages: longer wavelength LEDs require significantly thicker phosphor coatings for warm white lamps (Table 22). The thicker phosphor coating leads to additional scattering losses and lower efficacies. In Table 22, we normalize for LED WPE by taking the ratio of the lumen output by the LED optical power. The conclusions from this LED lamp test on these blends led us toward using LEDs with $\lambda_{max} < 452$ nm with these blends.

Table 22. Lamp testing using blue LEDs with GP3 and RP compositions detailing different wavelength light engines and coating thicknesses.

LED/coats	Lumens/blue optical watt	x	y	CCT	dbb	CRI
Engine 1 (449 nm)						
3 coats	169.36	0.3585	0.3049	4107	-0.057	78
4 coats	173.24	0.3708	0.3244	3829	-0.047	83
5 coats	176.52	0.4067	0.3679	3267	-0.024	88
6 coats	180.22	0.4358	0.4073	3046	0.003	90
Engine 2 (446 nm)						
3 coats	173.61	0.3727	0.3293	3819	-0.043	84
4 coats	176.30	0.3762	0.3386	3795	-0.036	86
5 coats	179.09	0.4152	0.3876	3265	-0.008	89
6 coats	181.39	0.4411	0.4235	3084	0.018	89
Engine 3 (460 nm)						
3 coats	152.43	0.3575	0.2834	3869	-0.078	49
4 coats	154.41	0.3633	0.2939	3750	-0.072	54
5 coats	158.15	0.4079	0.3357	2906	-0.057	66
6 coats	161.04	0.4376	0.3676	2672	-0.037	75

In these packages, the cool white (CCT~5000-6500 K; CRI~70-80) baseline using YAG:Ce-based phosphors are at 200-210 lumens/blue W(optical). Therefore, the performance of these warm white, 90+ CRI lamps are 85-90% of the cool white lamps, and the >25% gap between cool and warm white lamps is significantly reduced for warm white, high CRI (90+) lamps. Projecting this efficacy to a 50% WPE LED gives lamps with efficacies of ~91 lm/W. For a typical 3-chip device, this would translate into a ~300 lumen lamp at 3000 K, 90CRI. We extended these results further by taking making lamps using packages with 7-9 LED chips. Again, the best results were for LED modules that had a peak wavelength of <450 nm. In addition, the total phosphor efficiency in these packages was slightly lower than in the 3-chip lamps with the best efficiency of ~164 lm/blue W-opt at CCT=2880 K, CRI=90. Since these are instantaneous measurements, we believe that the additional losses for LED lamps with higher LED counts are due to additional package losses due to absorption by the LEDs themselves, which is exacerbated by the weaker GP3 absorption at $\lambda > 450$ nm. However, even with the current prototype designs, using 50% WPE LEDs would translate into lamps with an 83 lm/W efficacy at 2800-3000 K, CRI=90 and with a total lumen output of ~780 lumens for a 9 LED lamp.

Using the combination of GP3 and RP, many of the major efficacy deliverables and milestones for this program were met. However, as with the GP3, the RP phosphor is also sensitive to moisture (Figure 52). However, the RP materials appear to be much more sensitive to moisture versus GP3, possibly due to Mn hydrolysis and oxidation that causes a brown discoloration of the phosphor.

Figure 52. Picture of RP1 after high temperature/high humidity (HTHH) testing for 100 hours.

Moisture protection of phosphor powders

From the lamp reliability testing, we have found that two of our phosphors GP3 and RP have moisture sensitivity issues. These results motivated us to develop coatings and/or other methods to protect these phosphors in high temperature, high humidity (HTHH) environments. Initially, we focused upon the RP composition since its degradation was much more severe and because our initial reliability tests for GP3 showed no indication of moisture sensitivity (Table 19). Our first attempts to reduce the moisture sensitivity of RP were a treatment of the phosphor with various metal salts in isopropyl alcohol (IPA). These treatments somewhat improved the phosphor stability in HTHH environments (Figure 53), but while the discoloration of the phosphor was significantly less, there was still a significant loss (>50%) in the phosphor quantum efficiency after HTHH exposure. Therefore, we realized that any metric using sample discoloration alone was insufficient for determining any progress in RP protection. In addition, these coating/protection experiments involve a complicated interplay between phosphor, solvent, and coating/protection additives that can be difficult to rationally predict. In order to improve

the throughput of these experiment and to rapidly screen various coating/treatment strategies, we adapted some of our high-throughput screening (HTS) capabilities for both synthesizing coatings and evaluating their effectiveness with these experiments. Our initial test for the reproducibility and repeatability of these treatments in the HTS setup show a standard deviation of <5% in the plaque brightness, which is sufficient for initial screening experiments.

Figure 53. Picture of treated and untreated deep red phosphor after HTHH testing.

We investigated nanoparticle coatings to protect these phosphors against moisture and environmental degradation. One of our initial efforts has been with MgF_2 nanoparticles (Figure 54) precipitated with the deep red phosphor in solution. For these experiments, we initially observed an improvement in the stability of this phosphor under 85C/85%RH conditions (Figure 55). However, the morphology of these coatings showed that they did not completely coat the phosphor surface (Figure 56) and therefore were insufficient to completely protect the RP particles. Additional designed experiments for MgF_2 concentration, solvent, phosphor loading, and temperature did not lead to complete coating or significantly enhanced HTHH protection of RP particles.

Figure 54. XRD pattern of nanocrystalline MgF_2 used for coating deep red phosphor particles.

Figure 55. Relative efficiency of treated and untreated red phosphors before and after HTHH testing

Figure 56. Scanning electron micrograph of MgF_2 -coated RP particle. The blue regions denote Mg-rich regions that are due to MgF_2 nanoparticles.

Apart from nano-particle-based coating methodologies, we also attempted coatings/treatments of RP particles with long-chain molecules that are essentially surfactants to prevent condensation on RP phosphor particles. There are many different long-chain molecules that potentially could be used here, so the high throughput screening procedure help us to narrow down to a relevant set of molecules that showed significant improvements in the stability of RP when incorporated into GE Lumination silicones (Figure 57). Our initial testing of this coating method was for 0.5 g scale RP samples. We also scaled this process up for 10 g RP samples and measured similar stability in HTHH conditions. These samples are currently at GE Lumination for lamp and reliability testing.

Figure 57. Emission intensity versus exposure time to HTHH conditions for RP phosphor coated with long chain molecules incorporated into a GE Lumination silicone.

Our initial reliability results for the GP3 composition indicated no reliability issues in HTHH environments (Table 19), but modifications of this composition showed signs of degradation in white light blends at >2000 hours of HTHH LED testing (Table 21). We initiated additional effort to begin coating GP3 powders for HTHH protection. Since the degradation of GP3 is considerably slower than that of RP, we used environmental chamber conditions that accelerate the moisture degradation of GP3 to the point where the GP3 phosphor is completely destroyed after 100 hours of treatment (Figure 58). In our initial tests using different particle and sol-gel based coatings, we observe a significant improvement in the HTHH stability of GP3 versus the uncoated GP3 composition (Table 23). Since this is a significantly accelerated test, this level of protection could be sufficient for protecting GP3 from HTHH degradation in VioTM-like packages/prototypes. It is also important to note that while the VioTM package is not hermetically sealed, given the differences between HTHH stability of powders and devices, it likely provides some limited protection to the phosphor from HTHH conditions. We are currently making larger batches of the coated GP3 phosphor to test in VioTM-like packages/prototypes.

Figure 58. Plaque test of GP3 with Vio deep red phosphor before and after HTHH testing. This testing is comparatively accelerated versus the HTHH testing for the RP powders.

Table 23. Relative plaque efficiency for GP3 phosphor when blended with Vio deep red phosphor before and after HTHH testing. This testing is comparatively accelerated versus the HTHH testing for the RP powders.

Coating	% radiance
Uncoated	<1
Coating #1	30
Coating #2 (pH = 3)	29

Milestones for Task 4 - Incorporate phosphor materials into polymeric binders and composite processing

<5% loss in phosphor QE when incorporating initial compositions into GE Lumination polymer materials (4/2008)

To this point, in our plaque efficiency and phosphor decay time measurements, we have not measured any losses in phosphor efficiency when incorporating these phosphors into the current phosphor binder used in VioTM lamps. While we had phosphor reliability issues with GP1 and OP1, these reliability issues were due to inherent issues within the phosphor powder, not interactions with the silicone matrix.

<5% loss in phosphor QE when incorporating initial blends into GE Lumination polymer materials (4/2009)

We have continued our testing of our new phosphors within GE Lumination phosphor binders and have not seen any issues or additional losses due to the incorporation of these phosphors. However, we do observe some enhanced reactions at high temperature/high humidity for the GE Lumination deep red phosphor when it is incorporated into typical GE Lumination phosphor binders. Consequently, we have started work towards protection and/or coating of this phosphor. In addition, the lamp testing for our new phosphors (OP2, GP3) has not shown any sign of significant lumen loss or color shifts through at least 6,000 hours for initial samples and 1,000 hours for optimized samples. This is further evidence that there is little to no interaction between phosphor binders and silicones that reduce the QE of our new phosphors.

<5% loss in phosphor QE when incorporating final blends into GE Lumination polymer materials (7/2009)

As noted above, we have not measured any phosphor/polymer degradation when incorporating our new phosphors into typical GE Lumination phosphor binders. We have made progress in the protection of the GE Lumination deep red phosphor, and future lamp tests will indicate whether or not this will be sufficient for VioTM-like packages.

Milestones for Task 5 -Build and evaluate violet LED-based lamps

Phosphor blend development using new phosphors with blend luminosity of 330 lm/W-rad at CRI=80. (4/2008)

Verify CRI/CCT ranges for new blend development. (4/2008)

It is possible to have calculated phosphor blends using GP1 and OP1 that have very interesting spectral characteristics. However, since these phosphors have generally failed our initial reliability testing, we have not considered them within the milestones for this program. With the combination of GP3 and OP2, we are able to reach lumen equivalents of ~320 lm/W-opt at CRIs

of 83 for CCT=3000K. These lumen equivalents values are somewhat lower than our deliverable of 330 lm/W-opt, but this is natural considering that the CRIs are somewhat higher. We can lower this CRI, thereby raising the luminosity, by adding in OP3 to the blend composition, thereby reaching the luminosity of 330 lm/W-opt at CRIs of ~78. In addition, using internal GE Lumination red line emitting phosphors, it is also possible to reach lumen equivalents of 330 lm/W-opt at CCT=3000 K, CRI~90. Finally, when combining these new phosphors with the current materials in the GE Lumination portfolio, our models for spectral blending show that we are able to reach a full range of CCTs at CRIs ranging from 60-95.

Initial testing of new phosphor compositions for package efficiency & accelerated reliability; no loss in lumen output under accelerated reliability. (9/2008)

Package efficiency of optimized phosphor composition >10% vs. current phosphors. (9/2008)

One of the surprises within this program was the extremely poor reliability of some of our new phosphors, in spite of their high QE at room and elevated temperatures. Our initial testing in Vio™-like lamps showed reliability failures for OP1 and GP1 with very strong losses of >10% after <100 hours. This added another milestones in our phosphor downselection selection process to test in-house on powder plaques the initial reliability of new compositions. The next set of phosphors that were downselected passed our in-house plaque testing procedure at GE GRC for reliability (unlike OP1 and GP1) before further optimization begun. However, given the importance of reliability (and the relative difficulty to make accurate predictions for long-term behavior), we have put an initial focus for LED testing towards potential reliability issues. Our experience with OP1, GP1, and other phosphors that have failed LED reliability tests has been that factors such as the thickness of the phosphor coating or the phosphor particle size that could play an important role in the phosphor package efficiency are not critical factors in the phosphor reliability tests. Consequently, these factors were not addressed in these initial lamp tests. Our initial tests on OP2 and OP3 have gone out to >5000 hrs of testing in 405 nm packages, and we have observed no evidence for any lumen loss or color shifts for these materials, giving further confidence for downselection. We have also tested GP3 in reliability and have observed no reliability issues at ~8000 hrs of testing using blue LEDs and 5000 hours of testing with Vio LEDs. This testing is primarily for room temperature operation tests, so the positive results from these experiments allowed the team to have the confidence to further optimize these materials.

As noted above, we have not devoted significant resources towards these factors that govern the package efficiency of our new phosphors. However, the Lumination team has developed proprietary functions based upon the phosphor quantum efficiency, absorption, and thermal quenching that have accurately predicted the performance of modifications within the Vio package. Using these functions, we estimate that the steady-state package efficiency of OP2 at will be ~20% higher versus the current Lumination yellow phosphor, and the steady-state package efficiency of GP2 and GP3 will be ~25% higher versus the current Lumination blue-green phosphor. As discussed below, these estimates have been proven out in our lamp testing results.

Package efficiency of individual optimized phosphor compositions and blends 10% greater than current GELcore phosphors (9/2009)

Demonstration of 10% greater package efficiency for new phosphor blends + luminosity of 330 lm/W-rad (9/2009)

Lamp deliverable of >96 lm/W at 3000 K/CRI~80 & >71 lm/W at ~3000 K/CRI~95 when scaled to a 50% EQE LED chip (9/2009).

During Year 3 of this program, we have worked towards making blends and lamp testing of our new phosphors, including making optimized samples of these new phosphors for lamp testing. First, we have worked with blends of GP3 and OP2 as the green and red components and the standard GE Lumination blue phosphor for a tri-phosphor blend using 405 nm LEDs. We initially had to blueshift the color of GP3 through compositional modifications in order to have CRI>80 at CCT~3000 K. With this modification, we were able to achieve 55 lm/W efficacies (instantaneous) at CCT~3200K, CRI~81 using standard 405 nm LEDs in a three-chip Vio™ package. This is ~10% higher in efficacy when compared to standard Vio™ blends. In addition, while there is some improvement in pulsed measurements, there is an even larger improvement under steady state conditions where these new blends are ~20% higher in efficacy in three-chip Vio™ packages and ~40% higher in efficacy in six-chip Vio™ packages. These improvements are primarily due to the improved high temperature efficiency of these phosphors, since the phosphor temperature in Vio™ packages can reach 110°C and 130°C for three and six chip packages, respectively. In these blends, the blend luminosity is ~320 lm/W-rad, somewhat lower than our initial milestone. However, the enhanced high temperature efficiency offsets the ~3% lower lumen equivalent for the blue/GP3/OP2 blend. Finally, we have also gone through reliability testing for these blends in both room temperature operation (RTOL) and high temperature (85°C), high humidity (85% RH) (HTHH) testing. The OP2 phosphor shows no apparent signs of degradation or color shifts at 10,000 hours in both RTOL and HTHH testing using 3-chip Vio™-like packages. Our initial tests with the GP3 phosphor also have not shown any signs of degradation or color shifts at 7,000 hours in RTOL and HTHH testing. However, when appropriately modifying the composition of the GP3 phosphor to improve the color rendering in phosphor blends using OP2, there appears to be some degradation of this specific GP3 sample under HTHH conditions. We are currently evaluating this further since this result came towards the end of the program.

While the development of these tri-phosphor blends for 405 nm LEDs has been a major focus of this program, the invention of the GP3 family of phosphors with their inherent compositional and spectral flexibility allowed for blend development with 450 nm LEDs. The other main blend involved GP3 and a deep red line emitting phosphor that was internally developed by GE Lumination in combination with 450 nm LEDs. Using these phosphors, we are able to reach the blend luminosity goal of 330 lm/W-rad at CCT=2700-3000 K and CRI=87-92, depending upon the exact LED wavelength. Making a three LED lamp with 450 nm LEDs that have 43% wall plug efficiency (WPE), leads to a 270 lumen lamp with 82 lm/W efficacy at CCT=3000K, CRI~90 (R₉~80). At 50% WPE, this would translate into 3-chip, warm white lamps with >310 lumens at 95 lm/W. Apart from meeting the general program deliverables, these lamps have an efficacy that is ~90% of typical cool white lamps in similar packages, potentially closing the efficacy gap between cool white and warm white LEDs that use only phosphor downconversion.

4. Future work

Transition of phosphor synthesis to GE Lumination

Within this program, we developed small-scale (5-10 g/batch) synthesis procedures for OP2 and GP3 that were optimized using designed experiments. In addition, we also developed synthesis procedures for GP3 that we scaled up to 100 g batch sizes with additional process knowledge to understand some of the key control parameters that could limit any scale-up of this material. For OP2, the GE team has developed larger-scale synthesis procedures (outside of this program) that have been scaled up to 50 g batch sizes. At this point, standard synthesis procedures for OP2 and GP3 have been written, and these procedures have been tested at multiple sites within GE-GRC (outside of this program). Our next step is to transition these phosphor syntheses to GE Lumination. This transition has occurred for various phosphor systems in the past, and we have confidence in a smooth transition from GE-GRC to GE Lumination.

Moisture protection of phosphor powders

The lamp testing within this program has shown potential reliability issues with high temperature (85°C)/high humidity (85% RH) (HTHH) stability of the RP and GP3 compositions. There has been some progress towards improving the HTHH stability of these phosphors (Figure 57 and Table 23), but additional lamp testing is necessary to determine if these improvements are sufficient for using these phosphors in VioTM-like packages. If these improvements are not sufficient, it is clear that additional optimization work is necessary to improve the stability of these phosphors. Also, while it is important to pass HTHH testing, it is also unclear if any LED lamp used in general illumination will be subject to these relatively extreme conditions. Additional lamp/luminaire product definition will help to clarify these questions but is outside of the scope of this program.

Phosphor blend and package development

The lamp results discussed above are encouraging prototypes, but they also point towards the next steps required to maximize light engine efficacy. For example, in the 405 nm LED prototype (Figure 47), the phosphor coating thickness that maximizes lumen output still has a significant amount of violet radiation bleeding through the phosphor coating. Since the eye sensitivity to violet radiation is extremely low, this violet component is essentially equivalent to a loss in phosphor conversion efficiency and can be quantified by comparing the device luminosity with the phosphor luminosity. For example, the lamps made with violet LEDs typically had luminosities of 260-270 lm/W-rad versus a phosphor luminosity of ~320 lm/W-rad. Thicker phosphor coatings will absorb all of the violet radiation, but these thicker coatings have scattering losses that reduce the overall lumen output in spite of the complete absorption of violet radiation. We have already pointed out the blue phosphor used in these blends is designed for fluorescent lighting, making it sub-optimal for these devices. In addition, typical “white” circuit boards have significant absorption in the visible spectral region and relatively strong absorption in the near-UV, likely due to TiO₂ fillers (Figure 58). Removing this absorption would reduce the scattering losses from the phosphor coating and would allow for thicker phosphor coatings to improve conversion of violet LED radiation. These loss mechanisms are less severe in our blue LED light engines since some blue spectral component is needed to create white light, but since thicker phosphor coatings are needed to reduce the blue spectral component for warm white light CCTs, similar scattering losses are present. It is possible to “paint” these circuit boards with

white paint to remove this absorption (Figure 58), but we need to properly quantify the effects of improving circuit board/package reflectivity.

Figure 58. Reflectance of printed circuit board as received (C3.18 bare and TLG3 board) and painted.

Apart from optical losses within these light engines, there are also thermal issues that affect or arise from phosphor downconversion. Phosphors that quench at higher temperatures will subsequently heat up due to their lower QE, leading to more heat generation in the phosphor coating until steady-state conditions between this heating and any cooling process, such as conduction, natural convection, and radiation, are reached. The higher phosphor coating also heats the LED board and chip, giving LED wavelength shifts and an additional reduction in the LED chip efficiency. Some of these issues are addressed through improved phosphor compositions and synthesis processes, but the relationship between phosphor downconversion and light engine temperature is clearly demonstrated when comparing different phosphor blends in 6-chip Vio™ prototypes. Prototypes using our new phosphor blends with reduced thermal quenching have significantly lower board temperatures ($>15^{\circ}\text{C}$) versus the board temperature in typical 6-chip Vio™ devices (Figure 59). This reduction in light engine temperature from switching only the phosphor blend leads to an even larger improvement in LED efficacy beyond just higher phosphor QEs at elevated temperatures and points to a complex interaction between light engine design, phosphor composition, and steady-state performance.

Figure 59. Lumens and board temperature versus time for 6-chip Vio™ light engines. The higher QE at elevated temperatures for our new phosphor blends leads to less phosphor quenching and lower board temperatures, leading to much higher steady-state efficacies.

While scattering and thermal losses are significant in total, they are the product of many smaller losses within LED light engines and must be addressed to fully realize the benefits of optimized phosphor compositions. The eventual goal for phosphor and package designers will be to bring the steady-state phosphor conversion efficiency to that of linear fluorescent lamps, ~90%.

Fundamental understanding of phosphor reliability

Current DOE program goals require >50,000 hr lifetimes for warm-white LED luminaires. These long lifetimes will enable significant reductions in lamp replacement cost, reducing the overall cost of light. There has been significant work towards understanding the parameters for LED degradation, especially in regard to the LED junction temperature (T_j). The understanding of these effects has led to the design of different packages, lamps, and luminaires to minimize T_j . Despite the chemical robustness of many inorganic phosphors, degradation of phosphor performance can be one of the key contributors to efficiency loss over time, in part due to the extremely high (and increasing) photon flux from high power LED sources. We have screened and developed a number of phosphors with a wide range of reliability results, from phosphors that significantly degrade after <100 hrs of lamp testing to those that have passed >10,000 hrs of testing. However, many of the typical luminescence measurements in use for phosphor development (emission, excitation, efficiency, high temperature quenching, decay times) do not give reasonable predictors for phosphor reliability. As noted for the OP1 and GP1 compositions, it is likely that thermal ionization and color center formation play an important role in the degradation of these phosphors. We have additionally developed techniques using time-resolved spectroscopy to detect ionization processes within various luminescent materials through the detection of afterglow components (Figure 60). Since phosphor afterglow is dependent upon the trap structure as well as photoionization, this technique could be useful to help assess the formation of color centers in phosphors that show strong degradation.

Figure 60. Decay profile for $\text{Gd}_{0.999}\text{Ce}_{0.001}\text{ScO}_3$ ($\lambda_{\text{ex}}=320$ nm, $\lambda_{\text{em}}=440$ nm) versus temperature where the background has been subtracted from these decay profiles. Note the combination of a faster initial decay with an additional longer decay component at higher temperatures.

The lack of predictive capability for phosphor life in LED packages inevitably slows down the overall development cycle, since issues in phosphor life do not show up until well along the development path. It would be useful to use the materials and measurement capabilities developed in the GE/UGA programs to begin understanding the parameters that control phosphor reliability. This would aid in helping to guide phosphor chemists and material scientists towards

compositions and synthesis procedures to improve phosphor reliability as well as help to predict phosphor reliability out to 50,000 hr using shorter-term testing protocols.

5. Program management

DOE reports and presentations

All monthly, quarterly, and annual reports were filed as well as the required peer review report and presentation. At the 2008 DOE R&D workshop in Mesa, AZ, we made a poster presentation detailing the progress in our program. At the 2009 DOE R&D workshop in San Francisco, CA, we made a similar poster presentation as well as an oral presentation as part of receiving the “Illuminating Ideas” award from DOE. We also made a presentation on phosphor manufacturing at the Spring 2009 DOE Manufacturing Workshop in Fairfax, VA. Finally, we have made a poster presentation summarizing the entire program at the 2010 DOE R&D workshop in Raleigh, NC.

Filed patent applications

1. “Alkaline earth carboxylates as phosphor coatings to improve environmental resistance,” filed on 12/23/2009.
2. “Ce-doped Alkaline earth borate phosphors & use in LEDs,” filed on 12/02/2009.
3. “Cerium activated kimzeyite phosphor,” filed on 10/21/2009.
4. “Blue-green and green phosphors for lighting applications,” filed on 10/24/2008.
5. “Novel green emitting phosphors and blends thereof,” filed on 5/30/2007, published as US20080296596.

Patent disclosures in process/preparation

1. “Synthesis method for Ce^{3+} -doped phosphor,” disclosure filed on 1/6/2010.
2. “Coating moisture sensitive LED phosphors,” disclosure filed on 2/15/2010.

Peer-reviewed publications and conference proceedings

1. A.A. Setlur, C.S. Henderson, J.-H. Her, A.M. Srivastava, Nagaveni Karkada, N. Prasanth Kumar, E.V. Radkov, D. Aesram, A. Deshpande, B. Kolodin, L.S. Grigorov, and U. Happek, “High efficacy and color rendering light-emitting diode lamps using oxyfluoride and fluoride phosphors,” submitted for publication.
2. A.A. Setlur and U. Happek, “Cerium luminescence in nd^0 perovskites,” J. Sol. St. Chem, accepted for publication.
3. A.A. Setlur and J.J. Shiang, “Electron transfer between RE^{3+} ions in oxide hosts: experiments and quantitative analysis,” J. Phys. Chem. C **114**, 2792 (2010).
4. A.A. Setlur, “Phosphors for LED-based solid-state lighting,” Electrochemical Society Interface, Winter 2009, 32 (2009).
5. A.A. Setlur and J.J. Shiang, “Electron transfer between RE^{3+} ions in oxide hosts: experiments and initial quantitative analysis,” ECS Trans. **25**, 57 (2009).
6. U. Happek, A.A. Setlur, and J.J. Shiang, “Inverse bottleneck in Eu^{2+} - Mn^{2+} energy transfer,” J. Lumin., **129**, 1459 (2009).
7. A.A. Setlur, J.J. Shiang, M.E. Hannah, and U. Happek, “Phosphor quenching in LED packages: measurements, mechanisms, and paths forward,” Proc. SPIE **7422**, 74220E (2009).
8. U. Happek, M. Hannah, and A. Setlur, “Quenching of orange-red Ce^{3+} emission in garnet phosphors,” ECS Trans. **16**, 65 (2009).

9. A.A. Setlur and U. Happek, "Luminescence of Ce^{3+} in scandate perovskites," ECS Trans. **16**, 51 (2009).
10. A.A. Setlur, W.J. Heward, M.E. Hannah, and U. Happek, "Incorporation of Si^{4+} - N^{3-} into garnet hosts for warm white LED phosphors," Chem. Mater., **20**, 6277 (2008).
11. A.A. Setlur, A.M. Srivastava, H.L. Pham, M.E. Hannah, and U. Happek, "Charge creation, trapping, and long phosphorescence in $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$, RE^{3+} ," J. Appl. Phys. **103**, 053513 (2008).
12. A.A. Setlur, J.J. Shiang, and U. Happek, " Eu^{2+} - Mn^{2+} phosphor saturation in 5 mm light emitting diode lamps," Appl. Phys. Lett. **92**, 081104 (2008).