Next Generation Energy Efficient Fluorescent Lighting Product

Final Report

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NEXT GENERATION ENERGY-EFFICIENT FLUORESCENT LIGHTING PRODUCTS

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Energy Efficient Building Equipment and Envelop Technologies

Final report

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ABSTRACT

This is the Final Report of the Next-Generation Energy Efficient Fluorescent Lighting Products program, Department of Energy (DOE). The overall goal of this three-year program was to develop novel phosphors to improve the color rendition and efficiency of compact and linear fluorescent lamps.

EXECUTIVE SUMMARY

The prime technical approach was the development of quantum -splitting phosphor (QSP) to further increase the efficiency of conventional linear fluorescent lamps and the development of new high color rendering phosphor blends for compact fluorescent lamps (CFLs) as potential replacements for the energy-hungry and short-lived incandescent lamps in market segments that demand high color rendering light sources. We determined early in the project that the previously developed oxide QSP, $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}$, did not exhibit a quantum efficiency higher than unity under excitation by 185 nm radiation, and we therefore worked to determine the physical reasons for this observation. From our investigations we concluded that the achievement of quantum efficiency exceeding unity in $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}$ was not possible due to interaction of the Pr^{3+} 5d level with the conduction band of the solid. The interaction which gives rise to an additional non-radiative decay path for the excitation energy is responsible for the low quantum efficiency of the phosphor. Our work has led to the development of a novel spectroscopic method for determining photoionization threshold of luminescent centers in solids. This has resulted in further quantification of the requirements for host phosphor lattice materials to optimize quantum efficiency. Because of the low quantum efficiency of the QSP, we were unable to demonstrate a linear fluorescent lamp with overall performance exceeding that of existing mercury-based fluorescent lamps. Our work on the high color rendering CFLs has been very successful. We have demonstrated CFLs that satisfies the EnergyStar requirement with color rendering index (CRI) greater than 90; the CRI of current commercial CFLs are in the low 80s. In this report we summarize the technical work completed under the Program, summarize our findings about the performance limits of the various technologies we investigated, and outline promising paths for future work.

Program Goals and Benefits

The overall goal of this program was to reduce energy consumption and concurrently reduce pollution by developing novel phosphors to improve the color rendering and efficiency of compact and linear fluorescent lamps. By combining advanced phosphors and innovating system modeling for full optimization, we believe we can:

- further increase the efficiency of fluorescent lamps with the use of quantum-splitting phosphors which, on average, produce more than one visible photon for each incident ultraviolet photon.
- develop high color rendering (CRI>90) phosphor blends for compact fluorescent lamps as potential replacements for energy-hungry and short-lived incandescent lamps in markets that demand high color rendering light sources

The Next-Generation Energy-Efficient Fluorescent Lighting Product Program will provide benefit to the entire lighting industry and beyond. Achievement of the project goals will save money for US end-users, while the whole country will benefit from reduced energy consumption and pollution from fossil fuel power plants. The estimated reduction in national energy consumption through use of quantum splitting phosphors in linear fluorescent lamps is 0.1 quads while the estimated reduction in national energy consumption as a result of displacement of incandescent lamps by high-color-rendition compact fluorescent lamps is 0.03 quads. Therefore, the combined benefit of quantum splitting phosphors and high CRI CFLs is 1.03 quads. The estimated reduction in national carbon emission as a result of the use of quantum splitting phosphors in linear fluorescent lamps and displacement of incandescent lamps by high-color-rendition compact fluorescent lamps is 2 billion kilograms.

Technical Approach

Our project goals and the technical paths we have pursued are driven by our desire to closely approximate conventional fluorescent lamps in form, cost and manufacturing process. The technical path was also significantly impacted by the preferences of lamp customers. The quantum efficiency of the current fluorescent lamp phosphors is nearly 100 percent. We must, therefore, take into consideration the development of quantum splitting phosphors, which, on average, produce more than one visible photon for each incident ultraviolet photon if there is any hope of significantly increasing the efficacy of linear fluorescent lamps. Compact fluorescent lamps are three or four times as efficient as incandescent lamps of equivalent light output and can be used in many sockets that are currently fitted by incandescent lamps. However, the color rendering index in the middle 80s of current CFLs. An increase in the CRI of CFLs from the middle 80s to middle 90s has the potential of replacing incandescent lamps in markets sensitive to color rendition (such as retail, hotels and motels). The greater penetration of CFLs in commercial

markets is expected to produce substantial energy savings and concurrent reduction in pollution from fossil fuel powerplants.

COLLABORATIONS

Several major work were formally subcontracted outside GRC. The optical characterization of quantum-splitting phosphors which included the measurement of excitation and emission spectrum under vacuum ultraviolet radiation, the growth of single crystals and the determination of radiative and nonradaitive transitions was subcontracted to Prof. W. Yen and Prof. U. Happek at the University of Georgia. Dr. L. Shea at Sandia National Laboratory measured the relative quantum efficiency of the quantum-splitting phosphors. These subcontracted efforts will be detailed in the upcoming text.

I. QUANTUM SPLITTING PHOSPHORS

I.1 Introduction

About 25 years ago two research groups (GE and Philips) reported the observation of two photon emission processes. Piper et al demonstrated such a phosphor at GE GRC in 1974 [W. W. Piper, J. A. DeLuca and F. S. Ham, J. Lumin., 8, 344 (1974)]; this material consisted of Pr^{3+} in a host lattice of yttrium fluoride ($\text{YF}_3: \text{Pr}^{3+}$). The overall quantum efficiency under excitation by 185 nm radiation was ~ 1.7 . The process labeled photon cascade emission (PCE) or quantum-splitting can be described using Figure 1, which shows a portion of the electronic energy structure of the Pr^{3+} ion. Incident VUV photon is absorbed by Pr^{3+} from its ground state ($^3\text{H}_4$) into the Pr^{3+} 4f5d band. The state decays nonradiatively into the $^1\text{S}_0$ level. The $^1\text{S}_0 \rightarrow ^1\text{I}_6$ emission transition produced the first photon at 405 nm. A second nonradiative transition occurs, wherein lattice phonons allow a transition out of the $^1\text{I}_6$ level and into the nearby $^3\text{P}_0$ level. A second radiative transition then connects this upper level with several of the triplet levels lying within a few thousand wave numbers of the ground state. This results in a number of emission lines in the blue and red. The emission spectrum of this phosphor is shown in Figure 2.

Phosphor and discharge limitations precluded the commercial exploitation of the fluoride QSPs. Specifically, in low-pressure mercury lamps, the fluoride phosphors rapidly undergo discoloration during lamp operation. Also, the manufacture of the fluorinated materials is problematic because of environmental concerns and reactivity of fluorides.

The problems in the practical implementation of fluorides led GE to pursue the development of oxide host lattices which support quantum splitting. Pioneering research at GE led to the first observation of quantum splitting in oxide materials [A. M. Srivastava and W. W. Beers, J. Lumin., 71, 285 (1997)]. In the previous work on oxide QSPs we had codified a set of rules for the host lattice, which lead to the development of efficient quantum splitting action by the Pr^{3+} ion. From our present investigations of the efficiency of quantum splitting process in Pr^{3+} activated materials we conclude that the initial rules have to be modified in order to develop phosphors with quantum efficiency exceeding unity. In this respect, an important and unexpected finding was the photoionization of the Pr^{3+} center due to the overlap of the Pr^{3+} 4f5d band with the host lattice conduction band, which leads to additional nonradiative decay paths that reduces the quantum efficiency of the luminescent center. This will be discussed in detail in the section concerning the quantum efficiency of the $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}$ phosphor.

We also worked to develop methods of tailoring the luminescence of quantum splitting phosphors in a way that it contains the optimum wavelength for general lighting application. We co-doped $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}$ with green emitting Er^{3+} and observed the partial conversion of the Pr^{3+} emission in the far blue (lighting unfriendly spectral region) into more useful green emission. Although the energy transfer was far from optimum we

were successful in demonstrating the concept of spectral modification through the introduction of another activator ion.

Figure 1: The quantum splitting process in Pr^{3+} activated materials.

Figure 2: Room temperature emission spectrum of $\text{YF}_3:\text{Pr}^{3+}$ under 185 nm excitation

Table 1: Quantum efficiencies of the various transitions in $\text{YF}_3:\text{Pr}^{3+}$

Transition	Wavelength (nm)	Q E
$^1\text{S}_0 \rightarrow ^3\text{H}_4$	215.2	0.007
$^1\text{S}_0 \rightarrow ^3\text{H}_5$	225.4	0.001
$^1\text{S}_0 \rightarrow ^3\text{H}_6$	236.8	0.007
$^1\text{S}_0 \rightarrow ^3\text{F}_4$	251.7	0.053
$^1\text{S}_0 \rightarrow ^1\text{G}_4$	272.7	0.128
$^1\text{S}_0 \rightarrow ^1\text{D}_2$	338.2	0.015
$^1\text{S}_0 \rightarrow ^1\text{I}_6$	405.3	0.789
$^3\text{P}_0 \rightarrow ^3\text{H}_4$	484.3	0.210
$^3\text{P}_0 \rightarrow ^3\text{H}_5$	531.9	0.068
$^3\text{P}_0 \rightarrow ^3\text{H}_6, ^3\text{F}_2$	610.3	0.266
$^3\text{P}_0 \rightarrow ^3\text{F}_3, ^3\text{F}_4$	704.7	0.114
		$\Sigma = 1.66$

I.2 Theoretical quantum efficiency of $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}$ (SAP) quantum-splitting phosphor

This section will be devoted to a summary of the work performed as a part of the project on determining the quantum efficiency of the phosphor, $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}$.

One of the principle factor controlling the efficiency of the PCE process is the site symmetry of Pr^{3+} in the PCE phosphor. In a PCE phosphor, Pr^{3+} requires a site whose symmetry maximizes the $^1\text{S}_0 \rightarrow ^1\text{I}_6$ transition over the other $^1\text{S}_0$ transitions. The effect of the site symmetry on the $^1\text{S}_0$ branching ratio can be described using the Judd-Ofelt (J-O) phenomenological parameters for forced electric dipole transitions. Previous theoretical calculations have shown that the site symmetry that would maximize the $^1\text{S}_0 \rightarrow ^1\text{I}_6$ yield (and consequently the yield of the PCE process) over the other $^1\text{S}_0$ transitions would have J-O parameters such that $\Omega_2/\Omega_6=0$, $\Omega_4/\Omega_6=0$, and $\Omega_6 \neq 0$ [1]. We derived the J-O parameter ratios for SAP from the usual least squares fitting procedure on the absorption intensities of the Pr^{3+} ion in $\text{SrAl}_{12}\text{O}_{19}$ (for this purpose, single crystal fibers were grown by the technique) fitting the reduced matrix elements for Pr^{3+} to the visible absorption spectra using a least squares method. We, however, have neglected to take into account the spectral dependence of the index of refraction that is required in the estimation of the three Ω_k parameters.

This fitting gives J-O parameter ratios for Ω_2/Ω_6 and Ω_4/Ω_6 of 0.23 and 0.59, respectively. The relative probability of radiative transitions at various steps of the different emission process and as shown diagrammatically in Figure 3 is estimated from the aforementioned J-O parameters. The probability that initial radiative transition from the $^1\text{S}_0$ state yields a visible photon (transitions $^1\text{S}_0 \rightarrow ^1\text{I}_6, ^3\text{F}_2$) is determined to be $\eta_1 = 0.30$. The probability that the subsequent transition from the $^3\text{P}_0$ state will yield a visible photon is found to be $\eta_2 = 0.87$. In addition, although the initial quantum resulting from the transition $^1\text{S}_0 \rightarrow ^1\text{D}_2$ is in the ultraviolet (and therefore not useful) the probability that the subsequent transition from the $^1\text{D}_2$ state yields a visible photon (the transition $^1\text{D}_2 \rightarrow ^3\text{H}_4$) was found to be $\eta_2 = 0.6$. The probability that the system reaches the $^1\text{D}_2$ level after the initial decay from the $^1\text{S}_0$ state was determined to be $P_d = 0.10$. The total quantum yield (η_T) of the entire process is therefore given by:

$$\eta_T = \eta_1 (1 + \eta_2) + P_d \eta_3$$

For the aforementioned values of the various parameters, we obtain $\eta_T = 0.58$ for visible emission. For $\text{YF}_3:\text{Pr}^{3+}$ with $\Omega_2/\Omega_6=0.013$ and $\Omega_4/\Omega_6=0.070$, we obtain $\eta_T = 1.56$ for visible emission.

Figure 3: The relative probability of radiative transitions at various steps in the quantum splitting process

It is clear that the much-reduced efficiency of SAP ($\eta_T < 1$) is the result of having a large Ω_4/Ω_6 ratio (the Ω_4/Ω_6 ratio which is less than 0.25 is satisfactorily small). It is therefore clear that in order to obtain an efficient quantum splitting process we must incorporate the Pr^{3+} ion in a crystal site symmetry where the ratios Ω_2/Ω_6 and Ω_4/Ω_6 are close to zero. Note that in accordance with the larger Ω_4/Ω_6 ratio, the emission spectrum of SAP relative to $\text{YF}_3:\text{Pr}^{3+}$ is dominated by $^1S_0 \rightarrow ^3F_4, ^1G_4$ emission transitions. The strength of these transitions depends on the Ω_4 parameter, while the Ω_6 parameter determines the strength of the $^1S_0 \rightarrow ^1I_6$ transition. The intense UV emissions from the 1S_0 level in SAP reduce the visible quantum efficiency.

However, even with this reduction in the PCE process for SAP relative to YF_3 , we estimate that the total quantum yield greatly exceeds unity ($\sim 120\%$) when the UV photons originating from the 1S_0 state are taken into account. Of course, it is assumed

that the quantum efficiency of the 1S_0 emissions is unity, and that no concentration quenching occurs for either the 1S_0 or 3P_0 emissions.

I.3 Experimental estimation of quantum yield in $SrAl_{12}O_{19}:Pr^{3+}, Mg^{2+}$

In this section we focus on estimating the room temperature quantum efficiency of the SAP phosphor. The procedure for measuring absolute quantum efficiency is superficially straightforward, but fraught with possible systematic errors that must be thoroughly understood and eliminated. Consequently, the room temperature quantum efficiency of $SrAl_{12}O_{19}:Pr^{3+}, Mg^{2+}$ phosphor was estimated by comparing the integrated spectral power output of this phosphor with a sample of $YF_3:Pr^{3+}$ whose quantum efficiency has been previously measured by Piper et al. The measurements were carried out under identical luminescence detection parameters. The excitation wavelength was 185 nm. The ultraviolet reflectance of the powder samples (to determine how many ultraviolet photons are absorbed by the sample) was not measured and it was assumed that the reflectance is constant for both samples. This assumption is justified since the excitation spectra of the two samples are indicative of strong absorption (due to allowed $4f^2 \rightarrow 4f^1 5d$ transition) at 185 nm. Further, as we will see below, the quantum efficiency of the aluminate phosphor is so much lower than that of the fluoride material that small difference in the absorption of the primary VUV photon would have negligible consequence on the estimated quantum efficiency of the $SrAl_{12}O_{19}:Pr^{3+}, Mg^{2+}$ phosphor.

Table 2 summarizes the relative quantum efficiency of the various optical transitions emanating from the Pr^{3+} 1S_0 and 3P_0 states in $SrAl_{12}O_{19}:Pr^{3+}, Mg^{2+}$ and $YF_3:Pr^{3+}$ (from reference). These results indicate that the total [UV+ visible] and the visible quantum efficiency of the aluminate phosphor are only 42% and 27%, respectively and thus well below unity. The total and visible quantum efficiency of the $YF_3:Pr^{3+}$ phosphor are 165% and 145%, respectively.

To the extent that the Judd-Ofelt model predications are quantitatively accurate, we can immediately conclude from Table 2 that the model prediction of the total and visible quantum efficiency of $SrAl_{12}O_{19}:Pr^{3+}, Mg^{2+}$ is not confirmed experimentally. The assumption that the quantum efficiency of Pr^{3+} 1S_0 state in the PCE process is unity is clearly not valid. The observed discrepancy indicates an interesting and unexpected result: the quantum efficiency of the 1S_0 state in $SrAl_{12}O_{19}:Pr^{3+}, Mg^{2+}$, which is expected to be near unity, is in fact far below unity. Examination of Table 2 shows that the quantum efficiency of the 1S_0 state in $YF_3:Pr^{3+}$ is indeed close to unity.

This forgoing discussions suggests that nonradiative processes are operative on the 1S_0 state in $SrAl_{12}O_{19}:Pr^{3+}, Mg^{2+}$. In the next section we focus our attention on understanding the mechanisms controlling the nonradiative processes.

Table 2: The quantum efficiencies of the various transitions emanating from the 1S_0 and 3P_0 levels in Pr^{3+} activated $SrAl_{12}O_{19}$ and YF_3 .

Transition	$SrAl_{12}O_{19}:Pr^{3+}$	$YF_3:Pr^{3+}$
$^1S_0 \rightarrow ^3F_4$	4.6	5.3
$\rightarrow ^3F_4$	9.9	12.8
$\rightarrow ^3F_4$	0.9	1.5
$\rightarrow ^3F_4$	14.5	78.9
$^3P_0 \rightarrow ^3H_4$	5.9	21.0
$\rightarrow ^3F_4$	2.0	6.8
$\rightarrow ^3F_4$	4.2	26.6
REST	----	11.4

I.4 Temperature and concentration dependent non-radiative losses of energy from the 1S_0 and 3P_0 states in $SrAl_{12}O_{19}:Pr^{3+}, Mg^{2+}$

Examination of Figure 1 shows that only radiative return of the system from the 1S_0 state to the lower $^3P_2/^1I_6/^3P_1$ intermediate states must occur because of the rather substantial energy gap (about $24\,000\text{ cm}^{-1}$) between the starting and final levels. Consequently, the low quantum efficiency of the 1S_0 state may not be attributed to the bridging of the upper and lower states by nonradiative multiphonon relaxation processes.

The lifetime of the 1S_0 excited state as a function of temperature and Pr^{3+} concentration was measured to determine if the low luminescence efficiency is linked to temperature and concentration quenching factors. The decay times were determined by fitting the observed decay curves of the $^1S_0 \rightarrow ^1I_6$ optical transition to single exponentials. It was clear that the radiative decay time at 80 K and 300 K of two $SrAl_{12}O_{19}:Pr^{3+}, Mg^{2+}$ samples with significantly different Pr^{3+} concentrations, were little affected by the temperature. Thus, the low quantum efficiency of $Pr^{3+} ^1S_0$ state cannot be ascribed to a higher relative nonradiative transition probability at room temperature. We note that the observed decay time of about 600 ns is among the fastest intrinsic decay time that is observed for a 4f-4f

emission transition. The relatively fast decay is due to the close proximity of the opposite parity 4f5d band that mixes with the 1S_0 level, relaxing the parity selection rule.

It was shown in our previous work that concentration quenching of $Pr^{3+} ^1S_0$ emission in $SrAl_{12}O_{19}:Pr^{3+},Mg^{2+}$ only occurs when the activator ion concentration exceeds 10 mole per cent. Two reasons that a relatively high proportion of Pr^{3+} can be incorporated in the lattice without affecting concentration quenching are: (1) the lack of effective cross-relaxation pathways from the 1S_0 state, and (2) the large Sr^{2+} - Sr^{2+} nearest neighbor distance of ~ 5.6 Å in $SrAl_{12}O_{19}$ that minimizes effective interactions between mutual Pr^{3+} ions. Further the decay curve of the sample with 10 mole per cent Pr^{3+} does not deviate from single exponential and the decay time is not very different from the sample with 1 mole per cent Pr^{3+} at 80 K and 300 K. This indicates that concentration quenching is also not responsible (at least for Pr^{3+} concentrations of 1 per cent or less) for the low quantum efficiency of the $Pr^{3+} ^1S_0$ state in $SrAl_{12}O_{19}:Pr^{3+},Mg^{2+}$. The radiative decay time of the 3P_0 state is determined to be 36 μs . We also determined that the emission from the 3P_0 state is subject to concentration quenching since the measured decay times decreases with increasing temperature and with increasing Pr^{3+} concentration..

Let us now examine the variation of the $Pr^{3+} ^1S_0 \rightarrow ^1I_6$ emission intensity as a function of the temperature when the phosphor is excited by 185 nm-UV photon. Thermal quenching of the $Pr^{3+} ^1S_0 \rightarrow ^1I_6$ emission intensity is observed at temperatures beyond about 250 K. The emission intensity at room temperature has decreased to 80% of the low temperature value and is completely quenched by about 500 K.

In Figure 4 and we plot the variation of the $Pr^{3+} ^1S_0 \rightarrow ^1I_6$ emission lifetime and the intensity as a function of temperature. Examination of the data presented in these figures leads to the conclusion that while the lifetime of the 1S_0 emitting state remains constant from 20 K to 300 K the emission intensity steadily decreases as the temperature is raised beyond 250 K. Since the 1S_0 lifetime is practically independent of the temperature, mainly radiative processes determine its value. It is possible to qualitatively account for this experimental observation by assuming that nonradiative transitions proceed by a photoionization process involving the Pr^{3+} 4f5d localized state and the host lattice conduction band. In this model, which is discussed below, the 1S_0 state is not involved in the nonradiative transition. Note that the decay time of the $Pr^{3+} ^1S_0 \rightarrow ^1I_6$ emission is fairly independent of the temperature (Figure).

In the PCE process, as previously mentioned, the Pr^{3+} ion excited through the $4f^2 \rightarrow 4f^15d^1$ optical transition. The excitation then decays to the 1S_0 level by nonradiative means. The decrease in the $Pr^{3+} ^1S_0 \rightarrow ^1I_6$ emission intensity with increasing temperature may be interpreted as indicating that a part of the excitation energy from the lowest energy $4f^15d^1$ state relaxes (nonradiatively) to the 1S_0 state while a part of the excitation energy is lost nonradiatively. The first process results in the emission of the 405 nm photon ($^1S_0 \rightarrow ^1I_6$; see Figure 1). The experimental data suggest that as the temperature is increased to beyond 250 K more excited ions decay nonradiatively rather than spontaneously to the 1S_0 state. This implies a competition between the process that

populates the 1S_0 state and a process by which the excitation energy from the $4f^15d^1$ configuration relaxes nonradiatively to the ground state.

Figure 4 : (A) Dependence of the $^1S_0 \rightarrow ^1I_6$ emission intensity on temperature in SAP (B) Dependence of the $^1S_0 \rightarrow ^1I_6$ decay time on temperature in SAP and (C) Dependence of the $^1S_0 \rightarrow ^1I_6$ decay time on temperature in $YF_3:Pr^{3+}$

A direct nonradiative transition from the $4f^15d^1$ excited configuration to the ground state is not possible due to large energy gap between the initial and final states (see Figure 1). Hence the nonradiative probabilities must be such that all ions in the lowest energy excited $4f^15d^1$ state decay rapidly (and readily) to the 1S_0 state. Since the nonradiative decay of the excited $4f^15d^1$ state to the ground state cannot explain the experimental variation of the emission intensity with temperature and we are forced to consider another nonradiative mechanism.

An explanation for the thermal quenching of the 1S_0 state in $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}, \text{Mg}^{2+}$ involves the photoionization process which competes with the normal luminescence process. If the $\text{Pr}^{3+}4f^15d^1$ state is in proximity with the minimum of the host lattice conduction band it is possible for the Pr^{3+} ion to photoionize after excitation. Hence, after absorption of the incident VUV photons, the electron in the localized $4f^15d^1$ state is injected into the conduction band. This results in the formation of a delocalized electron in the conduction band (e_c) and a Pr^{4+} ion. The $[\text{Pr}^{4+} - e_c]$ state is referred to as an impurity bound excitation state in which the electron is delocalized in the host lattice and the hole trapped at the luminescent center.

Consequently, the two channels for relaxation of the $4f^15d^1$ state following optical excitation are the (nonradiative) relaxation to the 1S_0 state and the ionization process. The former process populates the 1S_0 level resulting in the emission of the 405 nm photon (and inducing subsequent emission from the 3P_0 level). The photoionization process decreases the number of ions relaxing to the 1S_0 level. Clearly, the relative importance of the two processes is temperature dependent; the ionization process becomes more efficient at higher temperatures (beyond 250 K). In this simple model, the decrease in the intensity of the $^1S_0 \rightarrow ^1I_6$ optical transition with increasing temperature should not be accompanied by a decrease in the lifetime of the excited state. This explains the remarkable lack of lifetime quenching of the $\text{Pr}^{3+} ^1S_0$ state when the luminescence efficiency decreases with increasing temperature.

In this study the problem of the fate of the electron residing in the conduction band is not resolved. The conduction band electron can relax nonradiatively to the $4f$ ground state of Pr^{4+} ion to reform Pr^{3+} . The decay is nonradiative since optical transitions representative of the $[\text{Pr}^{4+} - e_c]$ state is not observed. It is also possible that an exciton is formed whose energy is resonant with the 3P_0 intermediate states as has been found in the structurally related $\text{Sr}_{0.7}\text{La}_{0.3}\text{Al}_{11.7}\text{Mg}_{0.3}\text{O}_{19}:\text{Pr}^{3+}$ material. We postulate that the excitonic state empties partially into the lower energy $^3P_2/^1I_6/^3P_1/^3P_0$ intermediate states and more efficiently into the 3H_4 ground state. We now proceed to offer evidence for the direct and fast feeding of the 3P_0 state at 300 K under $^3H_4 \rightarrow 4f^15d^1$ excitation.

1.5 Analysis of the decay and rise time of the 1S_0 and 3P_0 states in $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}, \text{Mg}^{2+}$ and $\text{YF}_3:\text{Pr}^{3+}$

This section performs comparisons of the decay and rise times of the 1S_0 and 3P_0 states in $YF_3:Pr^{3+}$ and $SrAl_{12}O_{19}:Pr^{3+}, Mg^{2+}$ to gain further insights into nonradiative transitions issues which we had noted in the earlier section.

We note that in the PCE process a rise time should be associated with the 3P_0 state since upon VUV excitation the $^1S_0 \rightarrow ^1I_6$ optical transition populates the 3P_0 state. Figure 5 shows the single exponential decay of the 1S_0 state and the corresponding rise in the 3P_0 state following VUV excitation in $YF_3:Pr^{3+}$. It is observed that the 3P_0 rise and 1S_0 decay times are nearly equivalent at ~ 500 ns. This equivalence of the 1S_0 decay time with the 3P_0 rise time shows clearly that the only route to populate the 3P_0 level after VUV excitation of $YF_3:Pr^{3+}$ is through the radiative decay of the 1S_0 level, which is the first step in the photon cascade process for Pr^{3+} . In combination with the quantum efficiency values measured by Piper *et al.* [1], these measurements show that the quantum efficiency of the 1S_0 state of Pr^{3+} in YF_3 can be near unity, given proper synthesis conditions.

The analysis of time resolved measurements of the $SrAl_{12}O_{19}:Pr^{3+}, Mg^{2+}$ sample at room temperature show that the rise time of the 3P_0 luminescence under VUV excitation is significantly shorter than the decay time of the 1S_0 luminescence (Figure 5). In fact, there appears to be significant 3P_0 signal at $t < 10$ ns after the VUV laser pulse. This is in distinct contrast with our results with YF_3 , where the 3P_0 rise time is virtually equivalent to the 1S_0 decay time (Figure 3) and the signal starts at zero.

Consequently, there is a direct non-radiative decay pathway that directly populates the 3P_0 level after VUV excitation. We postulate that the state responsible for the direct feeding of the $^3P_2/^1I_6/^3P_1/^3P_0$ intermediate states is the impurity bound excitation state, $[Pr^{4+} - e_c]$. However, we do not see a significant change in the $^3P_0 \rightarrow ^3H_4/^1S_0 \rightarrow ^1I_6$ emission ratio at higher temperatures. We, therefore, postulate that the exciton like state predominately empties into the lower energy Pr^{3+} levels, perhaps directly into the 3H_4 ground state. It is also clear that the excitonic like state bypasses the 1S_0 state.

The decrease in the lifetime of the 1S_0 state at $T > 300$ K indicates the onset of nonradiative transitions. We also note that the decrease in the emission intensity of 1S_0 state follows the decrease in the lifetime of this state for $T > 300$ K. We propose that for $T > 300$ K, the 1S_0 state empties into the 4f5d state (upward transition) and that the direct ionization of 4f5d state (as previously discussed) is responsible for the decrease of the 1S_0 emission lifetime. Figure shows significant thermal broadening of the 4f5d excitation band at higher temperatures. This will reduce the energy difference between the 1S_0 and 4f5d states thereby increasing the probability for the promotion of an electron from the 1S_0 level to the bottom of the 4f5d band.

It is apparent from the temperature dependence of the 1S_0 emission of Pr^{3+} in SAP that there is significant quenching in our samples even at room temperature due to photoionization. Consequently, we believe that this quenching will reduce the quantum efficiency of $SrAl_{12}O_{19}:Pr^{3+}, Mg^{2+}$ under VUV excitation to the point where it will not be a viable phosphor for use in fluorescent lamps.

Figure 5: (A) Decay of the $^1S_0 \rightarrow ^1I_6$ emission in $YF_3:Pr^{3+}$ (B) Rise time of the 3P_0 state in $YF_3:Pr^{3+}$ and (C) Rise time of the 3P_0 state in SAP.

I.6 Quantum efficiency of the $LaMgB_5O_{10}: Pr^{3+}$ phosphor

The quantum efficiency of the $LaMgB_5O_{10}: Pr^{3+}$ quantum splitting phosphor was determined to be 42 percent despite the phosphor exhibiting favorable branching ratio for

the $^1S_0 \rightarrow ^1I_6$ transition. We failed to detect a TSLES signal when exciting by photons with wavelengths falling within the broad $\text{Pr}^{3+} 4f \rightarrow 5d$ excitation (absorption) band. From this data it was concluded that VUV excitation does not correspond to the ionization of the Pr^{3+} center in $\text{LaMgB}_5\text{O}_{10}$. Consequently, photoionization of the Pr^{3+} center cannot be responsible for the low quantum efficiency of this phosphor.

A factor that influences the luminescence efficiency of quantum splitting phosphors is the phonon frequency of the host lattice. Let us examine the room temperature emission spectrum of the oxide quantum splitting phosphor, $\text{LaMgB}_5\text{O}_{10}:\text{Pr}^{3+}$ (Figure 6). As previously discussed, the first photon in the quantum splitting process is generated by the $^1S_0 \rightarrow ^1I_6$ transition and the second photon by the efficient radiative decay to the ground state of the 3P_0 intermediate level. However, in contrast to $\text{YF}_3:\text{Pr}^{3+}$ and $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}$ the emission spectrum of $\text{LaMgB}_5\text{O}_{10}:\text{Pr}^{3+}$ shows the near absence of emission from the 3P_0 state. Instead the second photon transition produces weak emission in the red when excited with UV at room temperature. It is possible to associate this luminescence with the radiative return of the $\text{Pr}^{3+} ^1D_2$ state to the ground states; practically identical line spectra of luminescence is observed when exciting with photons of wavelength resonant with the $\text{Pr}^{3+} ^3H_4 \rightarrow ^1D_2$ absorption transition. We further note that the 3P_1 levels appear in the excitation spectrum of the 1D_2 fluorescence.

These results indicate that the intermediate 3P_0 level in $\text{LaMgB}_5\text{O}_{10}$ relaxes by multiphonon relaxation (non-radiatively) to the 1D_2 state. The interaction of Pr^{3+} ion with the host lattice phonons is responsible for the $^3P_0 \Rightarrow ^1D_2$ non-radiative relaxation process. The multiphonon relaxation rate can be given by the modified exponential energy gap law of Van Dijk and Schuurmans : $W_{\text{NR}} (T=0 \text{ K}) = \beta_{\text{el}} \exp [-\alpha(\Delta E - 2\hbar\omega_{\text{max}})]$ where β_{el} and α are constants for a given host lattice, ΔE is the energy gap and $\hbar\omega_{\text{max}}$ is the highest fundamental phonon frequency [9]. For borate glasses, $\beta_{\text{el}} = 16.8 \times 10^7 \text{ s}^{-1}$, $\alpha = 4.43 \times 10^{-3} \text{ cm}^{-1}$. With $\Delta E \approx 3300 \text{ cm}^{-1}$ and $\hbar\omega_{\text{max}} = 1400 \text{ cm}^{-1}$, we obtain $W_{\text{NR}} \approx 10^7 \text{ s}^{-1}$. Since the characteristic decay rate of the 3P_0 fluorescence in diluted systems (isolated Pr^{3+} ions) is $\sim 10^5 \text{ s}^{-1}$, the $^3P_0 \Rightarrow ^1D_2$ nonradiative relaxation process can compete with the radiative decay of the 3P_0 level. In $\text{YF}_3:\text{Pr}^{3+}$ where $\hbar\omega_{\text{max}}$ is of the order of $500 - 600 \text{ cm}^{-1}$, $W_{\text{NR}} \approx 10^2 \text{ s}^{-1}$ and so the $^3P_0 \Rightarrow ^1D_2$ nonradiative relaxation through multiphonon relaxation process is improbable in this case. Hence, the effectiveness of the $^3P_0 \Rightarrow ^1D_2$ nonradiative relaxation process in $\text{LaMgB}_5\text{O}_{10}$ (and LaB_3O_6) can be attributed to the high effective phonon energy ($\hbar\omega_{\text{max}}$) of the borate host lattice.

Without going into details, the probability that the system generates lighting useful visible photons from the 1D_2 state is lower than the probability of generating visible photons from the 3P_0 state. Thus far, no useful quantum splitting phosphors have been made from borates or phosphates because their lattices tend to exhibit high effective phonon energy so that a small number of phonons are required to bridge the $^3P_0 - ^1D_2$ energy gap via the multiphonon nonradiative process.

Figure 6: Room temperature emission spectrum of $\text{LaMgB}_5\text{O}_{10}:\text{Pr}^{3+}$ ($\lambda_{\text{ex}} = 185 \text{ nm}$)

I. 7 Color Correction studies of Pr^{3+} quantum-splitting phosphors

We have mentioned previously that the visible emission from is not directly suitable for use as white light source. As shown in Figure, the emission consists of a strong line in the deep blue near 405 nm from the initial radiative decay in the photon cascade process, and several weak lines near 484 nm and 610 nm which are perceived by the human eye as blue and red, respectively. The overall phosphor emission is therefore lacking in green, and the strong 405 nm (and UV emissions at shorter wavelengths) are essentially wasted because the human eye is virtually insensitive to that wavelength. An ideal improvement to the phosphor is to somehow shift the emission near 405 nm (and the strong UV emission arising from the $^1\text{S}_0 \rightarrow ^1\text{G}_4$ optical transition) closer to the peak in the eye sensitivity curve, around 555 nm in the green. This can be affected through codoping with other ions (such as rare earth ions) into the host lattice along with Pr^{3+} .

In order to accomplish the color correction, we codoped a new quantum splitting host material $\text{CaAl}_{12}\text{O}_{19}$ with Pr^{3+} and Er^{3+} and studied the Pr^{3+} to Er^{3+} energy transfer processes from 12 to 290 K. We have chosen Er^{3+} as a codopant because of its strong green emission and because some of its absorption transitions overlap the $^1\text{S}_0$ emission transition of the Pr^{3+} . We have indeed observed Pr^{3+} to Er^{3+} energy transfer in the $\text{CaAl}_{12}\text{O}_{19}$ (CAO) material and the partial conversion of ultraviolet emission transitions emanating from the Pr^{3+} $^1\text{S}_0$ state into useful green emission of the Er^{3+} ion. The efficiency of this energy transfer has been estimated based on the spectroscopic data and is of the order of 25% at room temperature.

Fig. 7: Room temperature excitation ($\lambda_{\text{ex}} = 205$ nm) and emission ($\lambda_{\text{em}} = 544$ nm) spectrum of CAO: Pr³⁺, Er³⁺ material

Figure 7 shows the excitation spectrum of CAO:Pr, Er when monitoring the Er³⁺ $^4S_{3/2}$ - $^4I_{15/2}$ emission transition (dashed line) and the total emission spectrum of the same sample under 205 nm excitation (solid line). For $\lambda_{\text{ex}} = 205$ nm, most of the emission transitions originates from the Pr³⁺ ion except for transitions in the 510 nm to 560 nm range, where the emissions of Pr³⁺ and Er³⁺ overlap. The detailed peak identifications are also shown in the figure.

It is clear from Fig. 7 that some of the 1S_0 and 3P_0 emissions of the Pr³⁺ ions coincide with the excitation lines of Er³⁺ ions. Specifically, Pr³⁺ emissions $^1S_0 \rightarrow ^3F_4$ at 253 nm, $^1S_0 \rightarrow ^1G_4$ at 273 nm, $^1S_0 \rightarrow ^1I_6$ at 401 nm, $^3P_0 \rightarrow ^3H_4$ at 486 nm, and $^3P_1/3P_0 \rightarrow ^3H_5$ at 520-550 nm, overlap Er³⁺ excitations $^4I_{15/2} \rightarrow ^4D_{7/2}$, $^4I_{15/2} \rightarrow ^2H_{11/2}(2)$, $^4I_{15/2} \rightarrow ^2H_{9/2}$, $^4I_{15/2} \rightarrow ^4F_{7/2}$, and $^4I_{15/2} \rightarrow ^2H_{11/2}(1)/^4S_{3/2}$, respectively. According to the Forster-Dexter theory [6,7], energy transfer from Pr³⁺ to Er³⁺ is possible under these resonant circumstances. The spectra (Fig. 7) indicate that the pair (Pr³⁺, Er³⁺) states (3P_0 , $^4I_{15/2}$) $\rightarrow$ (3H_4 , $^4F_{7/2}$) and ($^3P_0/3P_1$, $^4I_{15/2}$) $\rightarrow$ (3H_5 , $^4S_{3/2}/^2H_{11/2}$) are very likely the energy transfer paths. We believe that the additional transfer processes can involve 1S_0 as the initial state and we are currently trying to establish their importance.

One of the major factors affecting the transfer rate is the distance between the donor (Pr) and the acceptor (Er). The doped rare earth ions substitute Ca in the CAO host. Although the dopant concentrations are relatively high, the large molecule that contains only one Ca makes big separation between the donor and acceptor. The distance between the closest Ca sites is $a_0 = 0.5547$ nm [10], the smaller dimension of the unit cell in the host crystal. In the sample doped with 1% Pr and 5% Er, the average separation between

Pr and Er is a few nanometers. The large donor-acceptor separation results in a small interaction, giving a small energy transfer rate.

In conclusion, we have investigated the energy transfer processes in Pr^{3+} - and Er^{3+} -codoped CAO system. We observed the energy transfer from both $^1\text{S}_0$ and $^3\text{P}_0$ states of Pr^{3+} ions to Er^{3+} ions. UV excitation on Pr^{3+} was converted into the usable green emission of Er^{3+} .

There are drawbacks for Pr^{3+} quantum splitting in oxide lattices which prevent potential use as lamp phosphors. Either the Judd-Oflet parameters are unfavorable for high visible quantum efficiencies (as in SAP) or the phonon energy is too high leading to non-radiative decay from the $^3\text{P}_0$ to $^1\text{D}_2$ and cross-relaxation from that level leads to a low visible QE (as in the metaborates and pentaborates). These problems could be avoided by choosing the appropriate host lattice and dopants. The host lattice must have a significant amount of Gd^{3+} ions to allow for significant energy migration between Gd^{3+} ions. In addition, Mn^{2+} can be used as a co-dopant to trap any migrating energy and convert it into visible light. Previous rules devised for Pr^{3+} quantum splitting are still necessary for this process to work since quantum splitting would begin with absorption in the 4f5d band of Pr^{3+} and population of the $^1\text{S}_0$ state as before. There could be energy transfer between ions excited into the Pr^{3+} 4f5d band and Gd^{3+} ions, but this would be in competition with non-radiative decay into the $^1\text{S}_0$ state. In addition, there also direct energy transfer could occur between the $^1\text{S}_0$ state of Pr^{3+} and Gd^{3+} ions, but the spectral overlap between $^1\text{S}_0$ state of Pr^{3+} and the ^6G states of Gd^{3+} is small. For borate lattices, after the emission of the first photon, the Pr^{3+} ion non-radiatively decays into $^1\text{D}_2$ state. Energy transfer could occur between Pr^{3+} and Mn^{2+} (Figure 8) leading to a visible photon instead of cross-relaxation between Pr^{3+} ions. This would increase the visible QE for the borate quantum splitting phosphors and possibly allow for the use of other lattices with high phonon frequencies. In addition, the major UV emission transitions from $^1\text{S}_0$ could be converted into visible light using lattices that follow these rules. The $^1\text{S}_0 \rightarrow ^3\text{F}_4$ emission transition for Pr^{3+} has spectral overlap with the $^6\text{D}_J$ absorption transitions for Gd^{3+} , and the $^1\text{S}_0 \rightarrow ^1\text{G}_4$ emission transition for Pr^{3+} has spectral overlap with the $^6\text{I}_J$ absorption transitions for Gd^{3+} . Consequently, cross-relaxation can occur with Gd^{3+} ions (Figure 8), and this energy would then migrate across the Gd^{3+} sub-lattice until it reached a Mn^{2+} ion, which would then emit a green or red photon depending upon the crystal field at the Mn^{2+} ion. This could also significantly improve visible quantum efficiency. Potentially, two lattices that would satisfy all of the rules necessary for improved quantum splitting are $\text{La}_{1-x-y-z}\text{Gd}_x\text{Pr}_y\text{Mn}_z\text{B}_3\text{O}_6$, where $x > 0.5$ and $0.005 < y, z < 0.1$ and $\text{La}_{1-x-y}\text{Gd}_x\text{Pr}_y\text{Mg}_{1-z}\text{Mn}_z\text{B}_5\text{O}_{10}$, where $x > 0.5$ and $0.005 < y, z < 0.1$. For both host lattices, the crystal field is low at the RE^{3+} site, so that the 4f5d band for Pr^{3+} is above the $^1\text{S}_0$ level, an absolute necessity for quantum splitting to occur. There is sufficient Gd^{3+} in the sub-lattice to allow for percolation and energy migration between Gd^{3+} ions, and there is Mn^{2+} ions present to trap any energy migrating in the Gd^{3+} sub-lattice. We are unable at this point to identify the physical mechanism which would explain the ineffectiveness of the energy transport process in this system.

Figure 8. Schematic of the improved quantum splitting process. After population of the 1S_0 level, the majority of the radiative transitions are to the 1I_6 (the first visible photon), 1G_4 , and 3F_4 levels as before. Ions that radiatively relax from the 3P_0 level yield another visible photon. Any ions that non-radiatively relax from the 3P_0 to the 1D_2 level transfer their energy to Mn^{2+} giving a visible photon. The UV transitions from the 1S_0 level of Pr^{3+} to are converted into visible light by cross-relaxation with Gd^{3+} ions, energy migration across the Gd^{3+} sublattice, and trapping of that energy by Mn^{2+} , leading to visible photons. This figure simplifies the energy migration process by only showing migration over two Gd^{3+} ions. In reality, migration can take place over many Gd^{3+} ions.

I.8 New quantum-splitting phosphors

We successfully identified three new quantum-splitting phosphors based on the rules we had previously set forth. Quantum splitting was observed in $\text{CaAl}_{12}\text{O}_{19}$, $\text{CaMgAl}_{11.33}\text{O}_{19}$ and SrB_4O_7 . The room temperature emission spectrum of activated is shown in Figure. The observation of emission emanating from the $^1\text{S}_0$ state shows that the Pr^{3+} ion can quantum split the absorbed photon. As in the case of $\text{LaMgB}_5\text{O}_{10}$, the emission from the $^3\text{P}_0$ state is weak and strong relatively emission from the $^1\text{D}_2$ state is observed. The room temperature emission spectrum of Pr^{3+} activated $\text{CaMgAl}_{11.33}\text{O}_{19}$ is shown in Figure 9. The quantum-splitting phosphor $\text{CaAl}_{12}\text{O}_{19}$ is discussed elsewhere in the report.

Figure 9: The room temperature emission spectrum of Pr^{3+} activated SrB_4O_7 (top) and $\text{CaMgAl}_{11.33}\text{O}_{19}$ (bottom).

I.9 New quantum-splitting schemes

Quantum splitting in Pr^{3+} activated phosphor is only realized when the crystal field split components of the $\text{Pr}^{3+} 4f^1 5d$ configuration occur above the 1S_0 state. If this order is reversed (the lowest energy component of the $\text{Pr}^{3+} 4f^1 5d$ configuration is located below the 1S_0 state), the transition probability is such that the initial radiative transitions terminate into the lower energy $4f^2$ levels (3H_4 , 3H_5 , 3H_6 , 3F_2). However, if the emission transition from the 1S_0 state also terminates into the 3P_0 level, then a second photon can be generated when a transition occurs from the 3P_0 level to several of the triplet levels lying within a few thousand wavenumbers of the ground state.

The new quantum-splitting process can be described using Figure 10 , which shows the electronic structure of the trivalent Pr^{3+} ion. Note that the crystal field split components of the $\text{Pr}^{3+} 4f^1 5d$ configuration occur below the 1S_0 state. Quantum-splitting is realized by the generation of two photons corresponding to the $4f^1 5d \rightarrow ^1I_6(^3P_0)$ and $^3P_0 \rightarrow ^3H_J$ transitions, respectively. Since the bottom of the $\text{Pr}^{3+} 4f^1 5d$ configuration is a triplet, the $4f^1 5d \rightarrow ^1I_6(^3P_0)$ optical transition is spin allowed.

The Pr^{3+} ion was found to quantum split the incident 185 nm photon via this scheme in $(\text{Sr,Ca})\text{Al}_4\text{O}_7$ material. In this material, the lowest energy level of the $\text{Pr}^{3+} 4f^1 5d$ configuration is located below the 1S_0 state. Consequently, conventional quantum-splitting process, which starts from the 1S_0 state, is not anticipated in this material and indeed no emission from this upper state is observed. However, the emission spectrum upon excitation into the $4f \rightarrow 5d$ transition of Pr^{3+} contains a broad band upon which are superimposed some sharp line transitions (see Figure). The reverse $5d \rightarrow 4f$ transition terminating into the $^1I_6(^3P_0)$ states produces the broad band in the visible centered at about 490 nm. The sharp line emissions that are superimposed on the broad band are due to the $\text{Pr}^{3+} ^3P_0 \rightarrow ^3H_4$ transitions. This clearly demonstrates the generation of two visible photons through the aforementioned $4f^1 5d \rightarrow ^1I_6(^3P_0)$ and $^3P_0 \rightarrow ^3H_J$ transitions, respectively.

The drawback of this scheme of quantum splitting is related to the inefficiency of the $4f^1 5d \rightarrow ^1I_6(^3P_0)$ transition. The free-ion energy levels of the $\text{Pr}^{3+} 4f^1 5d$ configuration has been determined by Sugar, and for most of these the allowed electric-dipole selection rules would favor transitions to the lower energy levels of the $4f^2$, below 3P_0 . Nevertheless, we have demonstrated for the first time that it is possible to generate two visible photons in Pr^{3+} activated materials even when the levels of the $4f^1 5d$ configuration occur below the 1S_0 state.

Figure 10: Electronic energy scheme of the Pr^{3+} ion showing the $4\text{f}5\text{d}$ state at energies lower than the 1S_0 state (left) and the room temperature emission spectrum of $(\text{Sr,Ca})\text{Al}_4\text{O}_7$ ($\lambda_{\text{ex}} = 185 \text{ nm}$) under various excitation wavelengths (right).

I.10 Rules for discovery of efficient quantum-splitting phosphors

Previously we had designed a set of rules to identify oxide host materials in which Pr^{3+} can quantum split. It is clear from the work done under this program that the observation of quantum splitting does not also imply a quantum efficiency in excess of unity; all we can say is that non quantum splitting phosphors will never have quantum efficiencies above unity under low energy excitation. As we learned more about these materials and the conditions necessary for efficient quantum splitting, we refined a set of rules to optimize the quantum efficiency of the process. Perhaps the most important finding, which was not known at the outset of the program, was the discovery of photoionization of Pr^{3+} mediated by the interaction of the $4f^15d$ configuration with the extended states (conduction band) of the host lattice. This interaction is responsible for the low quantum efficiency of the quantum splitting process in $\text{SrAl}_2\text{O}_9:\text{Pr}^{3+}$ and prevents its use as a phosphor for higher efficacy fluorescent lamps.

The investigations on Pr^{3+} QSPs in this program has led us to modify our rules on the development of efficient Pr^{3+} QSPs. The entire set of rules which assist in identification of oxide quantum splitting phosphors as well as optimizing the quantum efficiency of then process are the following:

- Incorporating the Pr^{3+} ion in the host lattice so that the lowest energy bound states of the $4f^15d$ configuration are positioned above the 1S_0 state.
- Factors which determine the position of the lowest energy $4f^15d$ states are:
 - the coulomb interaction between the 4f and 5d electrons
 - the covalency effect, which causes a reduction in the coulomb energy due to expansion of the Pr^{3+} 5d orbitals in solids.
 - The crystal field splitting of the $4f^15d$ configuration, which additionally depresses the energy of the lowest crystal field level
- The host lattice band gap must exceed about 5 eV
- The vibrational frequency available for coupling to the rare earth ion must not exceed $\sim 800 \text{ cm}^{-1}$.
- **The position of the Pr^{3+} within the band gap of the host lattice must be such that the $4f^15d$ bands are not in resonance with the conduction band of the host lattice.**

Combining the modifications of the rules for Pr^{3+} quantum splitting with the energy transfer schemes developed in this program offers us a potential route for the development of phosphors with visible QEs >1 .

II. A NEW SPECTROSCOPIC TOOL FOR INVESTIGATING ELECTRON TRANSFER PROCESSES IN LUMINESCENT CENTERS: Thermally Stimulated Luminescence Excitation Spectroscopy (TSLES)

In connection with the aforementioned photoionization process, responsible for the less than unity quantum efficiency of the quantum splitting phosphor $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}$ there is a need for better experimental evidence rather than further speculations about the source of the photoionization process. A proper description of the photoionization process generally requires photoconductivity data and its interpretation in sufficient detail so as to determine the impurity ion energy level locations within the band gap of the host. A plot of the photoconductive response versus wavelength data yields optical photoionization energies of the luminescent center. In carrying out photoconductivity studies, it is hoped, to obtain information about the energy levels of the activator ions in the forbidden host-crystal energy regions.

The procedure for measuring photoconductive response is relatively straightforward when samples are available in the form of single crystal of high optical quality. However, when ceramic or polycrystalline samples (as in our case) are studied the photocurrent signal is too weak to be detected with sufficient accuracy and the procedure is fraught with possible errors that must be thoroughly understood and eliminated to obtain a qualitative and quantitative estimate. Additionally, the generation of parasitic currents at the electrodes limits the applicability of this technique to energies below 5 electron-volts.

Within the DOE program, we have developed a novel, universally applicable technique, which is based on thermo-luminescence spectroscopy (TLS) for the determination of optical photoionization energies of a luminescent center embedded in an insulating host crystal. This new technique can be regarded as a form of excitation spectroscopy and is termed Thermo-Luminescence Excitation Spectroscopy (TLES).

The fundamental nature of this novel technique (TLES) is shown in Fig. 11. In this figure, VB and CB represent the valence and conduction bands of the host-crystal. There are three main steps that must be performed to measure the photoionization energies. The first step involves the illumination of the sample at low temperatures by photons of fixed energy ($h\nu_E$) for a certain period of time. If the energy of the incident photon is sufficient to raise an electron to the conduction band (bridge the gap E_{PI} between the impurity ground state and the conduction band CB ;solid arrows, Fig 1a), a small fraction of the delocalized electrons will be trapped. If the incident photon energy is too small to bridge the gap (dashed arrow, Fig.1a), no electron transfer occurs and the traps remain empty. After illumination the sample temperature is rapidly raised and any trapped electrons are released due to thermal activation and recombine with the ionized impurities, with subsequent emission of impurity specific radiation at $h\nu_L$, i.e. TL is observed (Fig. 1b). The signal is recorded as a function of sample temperature, which is called the glow curve. The cycle is then repeated, illuminating the sample at a different wavelength. Plotting the integrated TL signal as a function of excitation wavelength then gives the ionization threshold of the impurity ion. Likewise, the threshold E_{CT} for charge transfer transitions can be determined.

To illustrate the principle of this technique, Figure 12 shows the glow-curves for a micro-crystalline sample of SAP. As previously mentioned the source of the low quantum efficiency was speculated to arise from the photoionization of the Pr^{3+} center in this material. Let us now examine the TSLES data. At an excitation wavelength of 250 nm the incident photon energy is too low to promote an electron into the host conduction band. Thus, traps are not filled and a TSL signal cannot be detected. At shorter excitation wavelengths (higher energies) the TSL signal rises, consisting of a single peak around 125 K. The observation of a TSL signal is an indication that the traps are filled via promotion of Pr^{3+} electrons into the conduction band. Integrating the TSL signals and plotting the result as a function of the excitation wavelength reveals the expected threshold behavior of the TSLES signal (Fig. 13). The signal rises abruptly 210 nm, which we interpret as the ionization threshold of Pr^{3+} . The abrupt rise in the TSLES signal coincides with the onset of the 4f5d absorption/excitation band. The TSLES technique that thus shows the creation of free charge carriers when exciting into the Pr^{3+} 4f5d band and unambiguously demonstrates the photoionization of the Pr^{3+} center in $\text{SrAl}_{12}\text{O}_{19}$.

It is clear that practical guides to efficient quantum splitting phosphors can be attained by focusing attention to understanding and controlling the nonradiative processes when the luminescence efficiency is low. This new spectroscopic technique that we developed has not only the immediate benefits in providing quantitative information on the mechanism and relative probabilities of radiative and nonradiative transitions but also in differentiating between electron and hole signals (nature of free charge carriers created during the ionization process) and has a much broader applicability to single crystals, ceramic materials and even noncrystalline materials (glasses) than the conventional photoconductivity technique.

Fig. 11: The fundamental principle of TSLES.

Fig. 12: Glow curves for SAP.

Fig. 13: TLES signal for SAP

III. HIGH COLOR RENDERING PHOSPHORS FOR COMPACT FLUORESCENT LAMPS (CFLs)

III. 1 Introduction

One of the major goals of this program focused on the development of high color rendering (CRI>90) phosphors blends for compact fluorescent lamps as potential replacement for energy-hungry and short-lived incandescent lamps in market segments that demand high color rendering light sources. The color-rendering index of high volume fluorescent lamps ranges from around 50 (halophosphate “Coolwhite” phosphor) to the mid 80s (rare earth based phosphors with emission in three narrow spectral bands). Since we are accustomed to judge colors by their appearance in daylight or blackbody sources (CRI=100 by definition), commercial markets that are sensitive to color rendition use incandescent lamps as light sources. Compact Fluorescent Lamps (CFLs) are three or four times as efficient as incandescent lamps of equivalent light output and are designed to fit into a conventional incandescent lamp socket. An increase in the CRI of CFLs from the middle 80s to middle 90s has the potential of replacing incandescent lamps in markets sensitive to color rendition. The greater penetration of CFLs in commercial markets is expected to produce substantial energy savings and concurrent reduction in pollution from fossil fuel powerplants.

With the above background, we can restate and discuss the project goal, which were stated in the original proposal and which were not substantially altered during the course of the work:

To develop high CRI (>90) phosphor blends for CFLs while simultaneously satisfying the EnergyStar requirement (>60 lumens/watt)

As an example, the CRI and efficacy of current 9 W CFLs which are available in several color temperatures, depending on the choice of the phosphor is shown in Table 3.

Table 3: CRI and efficacy of current commercial 9W CFL products

Color temperature	CRI	Lumens	LPW
2700	82	600	67
3500	82	600	67
4100	82	600	67

Figure 14: The emission spectrum of the “conventional” triphosphor fluorescent lamp blend with CRI= 82 (left) and the emission spectrum of a phosphor blend with CRI= 95 (right).

III.2 CRI of current commercial CFLs

It should be noted that while we can obtain good CRI with three narrow emission bands, saturated colors from yellow to deep red generally have sharply increasing reflectivity over the very narrow wavelength band, as shown in Figure 14. Consequently, the color of objects with a reflectance spectrum peaking in the region of the “holes” in the triphosphor emission spectrum (indicated by arrows in Figure 14) will be inferior when illuminated with a tricolor lamp relative to illumination with a blackbody source of the same color temperature. The goals for lamps with both high spectral efficacy and high color rendition were clarified by generating idealized spectra in wavelength range 390-750 nm. The CRI of the triphosphor lamps can be further improved by employing phosphors with broad emission bands. As shown in Figure 14, a blend of phosphors with emission spectrum that is very nearly flat from 450 nm to 700 nm, except for sharp lines of the mercury arc and those from the red emitting $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor (611 nm) yields a CRI of 95. However, when the color rendition is improved significantly, the lumen output is necessarily lower when using phosphors with broad emission bands. After the pertinent requirements have been specified, the technical challenge entails the development of a new phosphor blend that simultaneously satisfy the requirements of high efficacy (EnergyStar; LPW>60) and high CRI (>90).

III.3 New phosphors and blends for high CRI CFLs

A parameter critical to the operational lifetime of a CFL is the rate of decrease of the photoluminescence efficiency (lumen maintenance). Relative to linear fluorescent lamps, phosphors are subjected to higher wall loading in CFLs. Consequently, phosphors that are employed in linear fluorescent lamps may not necessarily exhibit high efficiencies in

CFLs. Thus, from a device standpoint it becomes necessary to determine the brightness and lumen maintenance of phosphors (and their blends) in lamps. We initially selected a specific CFL lamp type (lower wattage) and evaluated the brightness and lumen maintenance of twenty-five different phosphors (red, blue, green and blue-green emitting phosphors). This unique data base allowed us to recognize the phosphors that may lead to less-efficient lamps simply because of their poor lumen maintenance and helped us to settle on specific phosphors that met most nearly the requirements of high CRI, high efficacy CFLs. This database, in concert with the GE propriety phosphor system blending software, lead to realistic lamp performance predictions (lumens and CRI).

Spectral modeling for the attainment of high CRI shows that the upper limit on the color rendition which can be achieved depends critically on the wavelength of the red emission line. To achieve highest color rendition in the mid-90s the red emission wavelength must be near 621 nm. The lamp phosphor, $(\text{Gd,Ce})\text{MgB}_5\text{O}_{10}:\text{Mn}^{2+}$, whose emission spectrum is a broad band centered at 620 nm (Mn^{2+}), can be used to generate the required red light of the high CRI blend. However, the broad band emission is far from ideal. A narrow red emission would provide the desired color rendition while maintaining the highest luminosity of the blend. The narrow line emission spectrum near 620 nm of the lamp phosphor $\text{YVO}_4:\text{Eu}^{3+}$ is ideally suited for the practical realization of this principle. However, the phosphor has an unfortunate affinity for Hg, conducive to poor lamp performance. A new phosphor emitting a narrow line spectrum near 620 nm is thus required and critical to the development of CFLs with high CRI and high luminosity

Guided by these theoretical studies, a new deep red emitting phosphor consisting of a trivalent europium ion in a host lattice of gadolinium aluminate ($\text{GdAlO}_3:\text{Eu}^{3+}$) was discovered. The emission spectrum of this phosphor under 254 nm excitation is shown in Figure 15.

Figure 15: Room temperature emission spectrum of $\text{GdAlO}_3:\text{Eu}^{3+}$ under 254 nm excitation

The calculated CRI is 93 when this new deeper red emitting phosphor is blended with the appropriate blue, green and blue-green emitting phosphors. This represents a 10-point increase in the CRI over commercial CFLs. However, the unfavorable branching ratio of the Eu^{3+} emission leads to lower lumen output of the high CRI blend that utilizes the aluminate phosphor. Subsequently, we were able to discover two new deep red emitting phosphors with favorable branching ratio where the conditions of high CRI and high lumen output can be simultaneously satisfied.

During the program we were also successful in identifying and developing new yellow emitting phosphors, which in blends can lead to low color temperature CFLs.

Table 4 shows an example where $\text{CRI} > 90$ is attained at a color temperature of about 4100 K with a new phosphor blend (K21) which simultaneously satisfies the EnergyStar requirement ($\text{LPW} > 60$). The CRI of the standard 9W CFL is in the middle 80s. Also, note that the new phosphor blends show significant increase in the index of the red component (R9). We further point that some of the new phosphor blends can enable very high CRI (~ 95). However, such blends suffer from lower efficacy and do not meet the Energystar requirements.

Table 4: Lamp performance data of new phosphor blends (K21 and K 22B) that simultaneously satisfy the requirement of high CRI and Energystar

9W Bi-ax, blend with:	K 21	K 22 B	K 29	Standard
Measured data:				
Lamp voltage [AC V]:	60.2	60.6	60.1	61.3
Current [AC A]:	0.171	0.171	0.171	0.171
Power [AC W]:	8.672	8.705	8.6005	8.852
Luminous flux [lm]:	528.8	541.7	482.8	617.1
Light efficiency [lm/W]:	61.0	62.2	56.1	69.7
x =	0.3882	0.3767	0.3795	0.3760
y =	0.3949	0.3955	0.3956	0.3848
T _c =	3926	4222	4152	4178
R 1 =	90	90	92	95
R 2 =	93	91	94	92
R 3 =	81	81	74	57
R 4 =	94	92	95	90
R 5 =	97	96	97	86
R 6 =	95	91	93	80
R 7 =	94	92	96	92
R 8 =	80	82	96	78
R 9 =	34	38	71	18
R 10 =	89	85	78	48
R 11 =	95	93	91	75
R 12 =	92	90	84	57
R 13 =	87	85	89	94
R 14 =	86	86	82	71
R _a [1-8] =	91	89	92	84

PRESENTATIONS AT INTERNATIONAL CONFERENCES

- **Fall 2000 ECS meeting, Phoenix**

Optical transition probabilities for Pr^{3+} in $\text{SrAl}_{12}\text{O}_{19}$ and their relationship to the efficiency of the quantum-splitting process.

- **Spring 2000 MRS meeting, San Francisco (invited)**

Advances in the development of quantum splitting phosphors.

- **LS-9 meeting at Cornell University (invited)**

Recent developments in Multiphoton emitting phosphor for fluorescent lamps and display devices.

- **Fall 2001 ECS Meeting, San Francisco**

The efficiency of the quantum splitting process in $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}$.

- **Spring 2002 ECS meeting, Philadelphia**

On the efficiency of the photon cascade phosphor $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}$
Optical properties of the quantum splitting phosphor $\text{YF}_3:\text{Pr}^{3+}$

- **Erice Workshop on Luminescent Materials and Spectroscopy, Italy, July 2002 (invited)**

Recent advances in photon cascade emitting phosphors

- **International Symposium on Recent Developments in Inorganic Materials, Bombay, India, December 2002 (invited)**

Recent Developments in Multiphoton emitting phosphor for lighting and display applications

PUBLICATIONS

- ter Heerdt, M.L. H., Basun, S.A., Imbusch, G. F., and Yen, W.M., “Two- and three-photon excitation of Gd^{3+} in $CaAl_{12}O_{19}$ ”, J. Lumin. **100**, 115 (2001).
- ter Heerdt, M.L. H., van der Kolk, E., Yen, W.M., and Srivastava, A.M. “Vacuum ultraviolet spectroscopy of Pr^{3+} in $CaAl_4O_7$, $LaMgAl_{11}O_{19}$, and $SrLaAlO_4$ ”, J. Lumin. **100**, 107 (2001).
- Wang, X.J., Huang, S., Lu, L., Yen, W.M., Srivastava, A.M., and Setlur, A.A., “Energy transfer in Pr^{3+} - and Er^{3+} -codoped $CaAl_{12}O_{19}$ crystal”, Opt. Comm. **195**, 405 (2001).
- Wang, X.J., Huang, S., Lu, L., Yen, W.M., Srivastava, A.M., and Setlur, A.A., “Measurement of quantum efficiency in Pr^{3+} -doped $CaAl_4O_7$ and $SrAl_4O_7$ crystals”, Appl. Phys. Lett. **79**, 14 (2001).
- Huang, S., Lu, L., Jia, W., Wang, X.J., Yen, W.M., Srivastava, A.M., and Setlur, A.A., “The spectral properties of the 1S_0 state in $SrAl_{12}O_{19}:Pr^{3+}$ ”, Chem. Phys. Lett. **348**, 11 (2001).
- Huang, S., Wang, Xiao-jun, Meltzer, R. S., Srivastava, A. M., Setlur, A. A., Wen, Y., “The mixing of the $4f^2\ ^1S_0$ state with the $4f5d$ states in Pr^{3+} doped $SrAl_{12}O_{19}$ ”, Journal of Luminescence, **94-95**, 119-122, (2001)
- Fleniken, J, Grimm, M, Weber, J and Happek, U, “Thermally stimulated luminescence excitation spectroscopy (TSLES): a versatile technique to study electron transfer processes in solids”, Journal of Luminescence, **94-95**, 465-469 (2001)
- Happek, U, Choi, J and Srivastava, A. M., “Observation of cross-ionization in $Gd_3Sc_2Al_3O_{12} : Ce^{3+}$ ”, Journal of Luminescence, **94-95**, 7-9 (2001)

ISSUED PATENTS AND APPLICATIONS

Quantum Splitting Phosphors:

EP1258521A2 :Quantum-splitting oxide based phosphors

EP1258520A2 :Quantum-splitting oxide based phosphors

US20020171356A1 Quantum-splitting oxide-based phosphors, method of producing, and rules for designing the same.

Patent applications: Three additional applications have been submitted

High CRI CFL (applications):

Six applications have been submitted.