Yellow-Green Luminescence and Extreme Thermal Quenching in the $\text{Sr}_6\text{M}_2\text{Al}_4\text{O}_{15}:\text{Eu}^{2+}$ ($M = \text{Y, Lu, Sc}$) Phosphor Series

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Abstract

A series of Eu^{2+} -substituted yellow-green emitting phosphors based on the compound, $\text{Sr}_6\text{M}_2\text{Al}_4\text{O}_{15}$ ($M = \text{Y, Lu, Sc}$) were identified as potential efficient phosphors based on their high calculated Debye temperatures ($\Theta_D > 450$ K), which acts as a proxy for photoluminescent quantum yield (PLQY). The crystal structure contains corner-sharing $[\text{MO}_6]$ octahedra and $[\text{AlO}_4]$ tetrahedra leading to a highly connected, densely packed crystal structure. However, contrary to prediction, these compounds all showed a low PLQY ($< 6.5\%$) at room temperature. Temperature dependent luminescence measurements indicate that the photoluminescence is intense at 80 K but loses $\approx 90\%$ of the emission intensity by room temperature, with the thermal quenching temperature (T_{50}) occurring well below room temperature. These results suggest that even though Debye temperature (Θ_D) is a valid proxy for PLQY, it does not describe thermal quenching.

Introduction

Solid-state lights (SSL) are ideal to reduce energy consumption worldwide due to their high efficiency and long lifetimes, as compared to incandescent and compact fluorescent bulbs. Moreover, these devices are mechanically robust, chemically stable, small in size, and contain environmentally benign materials.[1] SSLs generally produce white light by combining the emission from a blue or near-UV light emitting diode (LED) with an inorganic phosphor that down-converts the absorbed light to longer wavelengths. The phosphors are composed of a host structure, often an oxide, that is substituted with a rare-earth luminescent center, like Ce^{3+} or Eu^{2+} . [2] When the rare-earth is coordinated by the host structure, the $5d$ orbitals of Ce^{3+} or Eu^{2+} crystal field split positioning them in an energy region allowing the $4f \rightarrow 5d$ electronic transitions to occur with visible light.[3] Combining the LED and phosphor emissions in the right ratio will cover the entire visible spectrum producing a functional white light.[4]

In the search for new efficient phosphors, recent design rules suggest that the phosphor host structure must be a crystallographically ordered, highly symmetric, structurally rigid compound.[5-7] This reduces the presence of non-radiative (vibrational) relaxation pathways, which negatively impact the photoluminescent quantum yield (PLQY).[8] Research has shown that an ideal descriptor for structural rigidity is the host crystal structure's Debye temperature (Θ_D), which can be determined using *ab initio* calculations combined with the quasi-harmonic Debye model.[9] A high Θ_D indicates a rigid crystal structure with limited non-radiative quenching mechanisms leading to a high PLQY.[10] Moreover, the compounds electronic band gap must be accounted for to ensure the desired electronic transition of the rare-earth ion is not impacted.

Using this methodology to screen compounds hosted within the Inorganic Crystal Structure Database (ICSD), a densely connected structure, $\text{Sr}_6\text{Y}_2\text{Al}_4\text{O}_{15}$, was identified. This compound along with its isostructural analogue $\text{Sr}_6\text{Lu}_2\text{Al}_4\text{O}_{15}$, are the only quaternary phases reported on their respective phase diagrams. [11] These compounds have been reported as efficient room temperature phosphors with some rare-earth luminescent centers. For example, Ce^{3+} -substituted $\text{Sr}_6\text{Y}_2\text{Al}_4\text{O}_{15}$ luminesces orange-red with a $\lambda_{\text{max}} = 600$ nm when excited at 460 nm.[12] $\text{Sr}_6\text{Y}_2\text{Al}_4\text{O}_{15}$ and $\text{Sr}_6\text{Lu}_2\text{Al}_4\text{O}_{15}$ have also been synthesized with Eu^{3+} resulting in the characteristic sharp emission lines between 570 nm and 720 nm that can be assigned to the various $4f \rightarrow 4f$ transitions of trivalent Eu.[13] Furthermore, $\text{Sr}_6\text{Y}_2\text{Al}_4\text{O}_{15}$ and $\text{Sr}_6\text{Lu}_2\text{Al}_4\text{O}_{15}$ co-substituted with Yb^{3+} and Ho^{3+} show up-conversion of a 980 nm excitation to an emission between 540 and 765 nm.[14] Other structural analogs, with the general formula $\text{Sr}_6M_2\text{Al}_4\text{O}_{15}$ ($M = \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}, \text{Tm}^{3+}, \text{and Yb}^{3+}$), have also been prepared although not investigated as phosphors.[15] Clearly, these compounds have potential as inorganic phosphors for solid-state lighting.

This report details the preparation and evaluation of three compounds that, when substituted with Eu^{2+} , are phosphors: $\text{Sr}_6\text{Y}_2\text{Al}_4\text{O}_{15}:\text{Eu}^{2+}$, $\text{Sr}_6\text{Lu}_2\text{Al}_4\text{O}_{15}:\text{Eu}^{2+}$, and the novel $\text{Sr}_6\text{Sc}_2\text{Al}_4\text{O}_{15}:\text{Eu}^{2+}$. The Θ_D of the host structures were first computed using *ab initio* calculations to predict their quantum yields and support the hypothesis that these compositions are viable phosphors. Their subsequent synthesis employed high temperature ceramic methods while the phase purity and crystal structure were confirmed using 11-BM synchrotron X-ray powder diffraction. Luminescence measurements reveal a weak yellow-green emission when excited with UV light at room temperature contrary to the predicted properties. However, temperature dependent measurements from 80 K to 300 K indicate thermal quenching by room temperature. These results challenge the practicality of the $\text{Sr}_6M_2\text{Al}_4\text{O}_{15}:\text{Eu}^{2+}$ ($M = \text{Y}, \text{Lu}, \text{Sc}$) series as phosphors; it also highlights the critical need for additional descriptors that account for thermal quenching to allow a comprehensive computational screening for novel phosphors.

Experimental Procedure

The Vienna *ab initio* Simulation Package (VASP), using the projector augmented wave method (PAW) and the generalized gradient approximation in the parametrization of Perdew, Burke, and Ernzerhof, was employed for all calculations.[16-19] A cutoff energy of 500 eV was chosen and a $2 \times 8 \times 8$ Γ -centered Monkhorst-Pack k -point grid was used. To find the electronic ground state of the structures, the atomic positions, lattice parameters, and unit cell volumes were allowed to relax with an electronic convergence criterion of 1×10^{-6} eV until the forces were below 0.01 eV/Å per cell. Stress tensor calculations were carried out on the fully relaxed structures with an energy cut-off of 600 eV. From the resulting elastic moduli, Θ_D was approximated using the quasi-harmonic Debye model.[10, 20, 21]

Polycrystalline samples of $\text{Sr}_6M_2\text{Al}_4\text{O}_{15}$ ($M = \text{Y}, \text{Lu}, \text{Sc}$) with Eu^{2+} substituted for the Sr^{2+} , e.g. $(\text{Sr}_{1-x}\text{Eu}_x)_2M_2\text{Al}_4\text{O}_{15}$ ($M = \text{Y}, \text{Lu}, \text{Sc}; x = 0, 0.0025, 0.005, 0.01, 0.02, 0.03, 0.05$), were prepared by high-temperature solid state reaction. The starting materials: SrCO_3 (99% Alfa Aesar), Y_2O_3 (99.9% Alfa Aesar), Lu_2O_3 (99.9% Materion Advanced Chemicals), Sc_2O_3 (99.9% Materion Advanced Chemicals), Al_2O_3 (99.99% Sigma-Aldrich), and Eu_2O_3 (99.9% Materion Advanced Chemicals) were weighed out in the correct stoichiometric ratios and mixed using an agate mortar and pestle for approximately 30 minutes. BaF_2 and NH_4Cl were incorporated (1 wt%) as fluxes. The starting materials were pressed into pellets and placed in an alumina crucible (AdValue Technology) on top of sacrificial powder. The samples were heated to 1450°C under flowing 5% H_2 /95% N_2 at a rate of 3°C/min, held at temperature for 12 hours, and then cooled to room temperature at a rate of 3°C/min.

The resulting products were ground to a fine powder using an agate mortar and pestle. High-resolution synchrotron X-ray powder diffraction was carried out on the 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory.[22, 23] The data were collected at room temperature with a

calibrated wavelength of $\lambda = 0.413844 \text{ \AA}$ for $M = \text{Y, Lu}$ and $\lambda = 0.414174 \text{ \AA}$ for $M = \text{Sc}$. Rietveld refinements of the data were performed using the EXPGUI interface for the General Structure Analysis System (GSAS).[24, 25] A shifted-Chebyshev function was used to fit the background and a pseudo-Voigt function to fit the peaks.

Temperature dependent photoluminescence spectra were measured using a PTI QuantaMaster with a 75 W xenon arc lamp for excitation and a Janis VPF-100 liquid nitrogen cryostat for temperature controlled measurements between 80 K and 300 K. Quantum yields were measured using a 150 mm SpectralonTM-coated integrating sphere. Each sample was mixed with silicon resin (GE Silicones, RTV615) and placed on a quartz substrate (Chemglass) for measurement. The external PLQY was calculated based on the method of de Mello *et al.*[26]

Results and Discussion

Computationally screening the ICSD for highly connected crystal structures that have a high Θ_D highlighted the compound $\text{Sr}_6\text{Y}_2\text{Al}_4\text{O}_{15}$ as a potential phosphor host.[11] Two isostructural analogues with the general composition $\text{Sr}_6M_2\text{Al}_4\text{O}_{15}$ ($M = \text{Y, Lu}$), which have been experimentally reported, as well as the hypothetical $M = \text{Sc}$ compound, which was initialized using the known structure then optimized, were examined using density functional theory. Owing to their identical structural connectivity, the calculated Θ_D for all three compounds are similar with the $\text{Sr}_6\text{Y}_2\text{Al}_4\text{O}_{15}$ $\Theta_D = 468 \text{ K}$, the $\text{Sr}_6\text{Lu}_2\text{Al}_4\text{O}_{15}$ $\Theta_D = 448 \text{ K}$, and the $\text{Sr}_6\text{Sc}_2\text{Al}_4\text{O}_{15}$ $\Theta_D = 524 \text{ K}$. These calculated values are comparable to a number of known efficient Eu^{2+} -substituted phosphor hosts such as $\text{BaLu}_2\text{Si}_3\text{O}_{10}$ (500 K),[27] $\alpha\text{-Sr}_2\text{SiO}_4$ (428 K), Ba_2SiO_4 (307 K),[28] and $\text{Sr}_2\text{BaAlO}_4\text{F}$ (466 K),[10] signifying their potential to exhibit a high PLQY. Furthermore, the calculated band-gap, determined using the HSE06 hybrid functional due to its balance between accuracy and computational cost, [29] showed a direct bandgap 5.66 eV for $\text{Sr}_6\text{Sc}_2\text{Al}_4\text{O}_{15}$, 5.75 eV for $\text{Sr}_6\text{Lu}_2\text{Al}_4\text{O}_{15}$, and 5.80 eV for $\text{Sr}_6\text{Y}_2\text{Al}_4\text{O}_{15}$ supporting that even though these compounds are highly connected, they maintain a wide band-gap allowing the required electronic transitions. Thus, they are valid targets for experimental exploration.

Synthesis and Structure Determination

The synthesis of the three phases, $\text{Sr}_6M_2\text{Al}_4\text{O}_{15}$ ($M = \text{Y, Lu, Sc}$), used a high temperature ceramic route starting from the oxide powders. According to a Rietveld refinement of the synchrotron X-ray powder diffractograms, shown in Figure 1, the reaction at 1450°C for 12 hours under reducing conditions produced phase pure $\text{Sr}_6\text{Y}_2\text{Al}_4\text{O}_{15}$ while the $M = \text{Lu}$ and Sc analogues both contained a small amount of unreacted $M_2\text{O}_3$ starting material (less than 6 mole percent as determined by Rietveld refinement) .

Because of the low substitution concentration, Eu^{2+} was disregarded in the structural refinement. The cell parameters and refinement results for all three phases are listed in Table 1.

Figure 1. Rietveld refinements of (a) $\text{Sr}_6\text{Y}_2\text{Al}_4\text{O}_{15}$, (b) $\text{Sr}_6\text{Lu}_2\text{Al}_4\text{O}_{15}$, and (c) $\text{Sr}_6\text{Sc}_2\text{Al}_4\text{O}_{15}$ using synchrotron X-ray powder diffraction data. The measured data are shown in black, the fit by the yellow line and the difference between the data and the fit by the blue line.

Table 1. Structure refinement data for $\text{Sr}_6\text{Y}_2\text{Al}_4\text{O}_{15}$, $\text{Sr}_6\text{Lu}_2\text{Al}_4\text{O}_{15}$, and $\text{Sr}_6\text{Sc}_2\text{Al}_4\text{O}_{15}$ obtained using the Rietveld method on synchrotron X-ray powder diffraction data.

formula	$\text{Sr}_6\text{Y}_2\text{Al}_4\text{O}_{15}$	$\text{Sr}_6\text{Lu}_2\text{Al}_4\text{O}_{15}$	$\text{Sr}_6\text{Sc}_2\text{Al}_4\text{O}_{15}$
radiation type, λ (Å)	synchrotron (11-BM), 0.413844	synchrotron (11-BM), 0.413844	synchrotron (11-BM), 0.414174
2θ range (deg)	0.500 – 49.992		
temperature (K)	295		
crystal system	monoclinic		
space group; Z	$C2_1$; 2		
lattice parameters (Å)	$a = 17.59056(3)$	$a = 17.47765(4)$	$a = 17.24642(5)$
	$b = 5.73933(1)$	$b = 5.91309(1)$	$b = 5.63150(1)$
	$c = 7.68449(2)$	$c = 7.63986(2)$	$c = 7.56651(2)$
β (°)	90.7790(2)	90.9242(2)	91.3196(3)
vol. (Å ³)	775.740(2)	762.752(2)	734.689(3)
R_p	10.28	9.93	10.43
R_{wp}	13.70	12.76	13.60

R_f^2	6.23	5.24	7.85
χ^2	4.22	3.74	3.03

Figure 2. Structure of $\text{Sr}_6\text{M}_2\text{Al}_4\text{O}_{15}$ ($M = \text{Y}, \text{Lu}, \text{Sc}$) featuring a corner-connected chain of $[\text{AlO}_4]$ tetrahedra and $[\text{MO}_6]$ octahedra. The four crystallographically independent Sr^{2+} positions are highlighted.

$\text{Sr}_6\text{M}_2\text{Al}_4\text{O}_{15}$ ($M = \text{Y}, \text{Lu}, \text{Sc}$) crystallizes in the non-centrosymmetric monoclinic space group, $C2$ (No. 5) with refined cell parameters that increase from Sc^{3+} through Y^{3+} following the increase in the M ion radii (Y^{3+} , $r_{6\text{-coord}} = 0.900 \text{ \AA}$; Lu^{3+} , $r_{6\text{-coord}} = 0.861 \text{ \AA}$; Sc^{3+} , $r_{6\text{-coord}} = 0.745 \text{ \AA}$).^[30] The refined atomic positions are provided in Table S1 of the Supporting Information. The crystal structure of $\text{Sr}_6\text{M}_2\text{Al}_4\text{O}_{15}$ (Figure 2) consists of corner-connected $[\text{AlO}_4]$ tetrahedra and $[\text{MO}_6]$ octahedra in an alternating fashion forming an infinite chain along the a -axis. The connection between these polyhedra produces a three-dimensionally connected network that likely leads to the high calculated Debye temperatures. As the M ionic radius decreases from Y^{3+} to Sc^{3+} , the $[\text{MO}_6]$ polyhedral volume decreases from $15.00 \text{ \AA}^3$ ($M = \text{Y}^{3+}$) to $14.58 \text{ \AA}^3$ ($M = \text{Lu}^{3+}$) to $12.68 \text{ \AA}^3$ ($M = \text{Sc}^{3+}$). The structure contains four crystallographically independent Sr^{2+} sites as well; Sr(1), located at Wyckoff position $4c$ is surrounded by ten oxygen atoms, Sr(2) at Wyckoff position $4c$ forming a $[\text{SrO}_9]$ polyhedra. Sr(3) forms a ten coordinate $[\text{SrO}_{10}]$ polyhedra and is located in the more symmetric Wyckoff position $2a$ while Sr(4), forms a $[\text{SrO}_8]$ polyhedra and is located on Wyckoff position $2b$. These Sr-centered polyhedra are decorated among the network of $[\text{AlO}_4]$

tetrahedra and $[MO_6]$ octahedra with primarily face-sharing connectivity, which further aids in the formation of a dense structurally rigid network and high-calculated Debye temperatures.

Optical Properties

The un-substituted samples ($x = 0$) were first measured using diffuse reflectance (Figure S1) to confirm the predicted bandgaps. The samples possess experimentally measured (direct) bandgaps of 5.12 eV for $Sr_6Sc_2Al_4O_{15}$, 5.38 eV for $Sr_6Lu_2Al_4O_{15}$, and 5.66 eV for $Sr_6Y_2Al_4O_{15}$, which are in excellent agreement with the calculated bandgaps. To prepare the phosphor, Eu^{2+} was substituted following the general formula $(Sr_{1-x}Eu_x)_6M_2Al_4O_{15}$ ($x = 0, 0.0025, 0.005, 0.01, 0.02, 0.03, 0.05$). The subsequent optimization of the Eu^{2+} , identified based on room temperature PLQY, indicate the best samples had a low rare-earth concentration ranging between 0.25% ($x = 0.025$) and 0.5% ($x = 0.05$) after which quenching is apparent (Figure S2 of the Supporting Information). Surprisingly, the optimized PLQY for $(Sr_{1-x}Eu_x)_6Y_2Al_4O_{15}$ is <6.5% ($x = 0.065$; $\lambda_{ex} = 365$ nm) contradicting the high predicted efficiency based on the Debye temperature.

Nevertheless, the compositions all exhibit a broad excitation spectrum spanning from the deep UV (<300 nm) to the near UV (≈ 410 nm), shown in Figure 3. Exciting at 365 nm yields an emission in the yellow-green region of the visible spectrum with $\lambda_{max} = 530$ nm ($M = Y$), 524 nm ($M = Lu$), and 525 nm ($M = Sc$), presented in Figure 3, while exciting at 405 nm produces a nearly identical emission. The luminescence arises from the allowed $^7H_j \rightarrow ^1S_1$ transitions in Eu^{2+} . Interestingly, it is not possible to resolve the four crystallographically independent luminescent centers due to strong vibronic coupling at room temperature generating a broad emission spectrum. There is also a slight discontinuity in the emission peak shape of $M = Y$ and $M = Lu$ at ≈ 600 nm. The luminescent center, Eu^{2+} ($r_{6-coord} = 1.17$ Å), is expected to substitute primarily on the Sr^{2+} ($r_{6-coord} = 1.18$ Å) site because of their similar ionic radii and isovalency.[30] However, the radii of 6-coordinated Eu^{3+} ($r_{6-coord} = 0.947$ Å) is also comparable to Y^{3+} and Lu^{3+} allowing potential substitution of the rare-earth on the M^{3+} site as well. Comparing these emission curves to $M = Sc^{3+}$, an ion that produces a polyhedra too small for Eu^{3+} to occupy, the absence of this anomaly supports that the signal arises from a mixed valence rare-earth.

Figure 3. Excitation (blue) and emission (green) spectra for (a) $\text{Sr}_6\text{Y}_2\text{Al}_4\text{O}_{15} : 3\% \text{Eu}^{2+}$, (b) $\text{Sr}_6\text{Lu}_2\text{Al}_4\text{O}_{15} : \text{Eu}^{2+}$, and (c) $\text{Sr}_6\text{Sc}_2\text{Al}_4\text{O}_{15} : \text{Eu}^{2+}$. All compounds are excited at 365 nm. A color bar is shown above for reference.

Integrating the emission spectra over the tri-stimulus function, the CIE coordinates are plotted on a 1931 CIE diagram in Figure 4[31] shows the yellow-green luminescence for the compounds. According to crystal field theory, as the unit cell volume decreases following the changing M ion radius, the luminescence should red shift; however, this is contrary to what is observed here with the data actually blue shifting.[32] This surprising trend arises from changes in the full-width at half of the maximum intensity (FWHM) of the emission spectra. Although the onset of luminescence for all three compounds begins at nearly the same wavelength, the FWHM of the emission spectra are very different. For $M = \text{Y}$, the luminescence extends well into the red region producing a broad emission spectrum with a FWHM of

3666 cm^{-1} . The emission spectrum of $M = \text{Lu}$ is narrower with a FWHM of 3138 cm^{-1} and ends at a shorter wavelength compared to the yttrium analog while the narrowest emission spectrum, and thus the most blue-shifted, belongs to the compound with the smallest $M = \text{Sc}$ with a FWHM of 2754 cm^{-1} . The large FWHM of $M = \text{Y}$ and $M = \text{Lu}$ likely arises from a combination of multiple luminescent centers as well as the presence of red-emitting Eu^{3+} .

Figure 4. The room temperature CIE coordinates for $\text{Sr}_6\text{Y}_2\text{Al}_4\text{O}_{15}:\text{Eu}^{2+}$ (square), $\text{Sr}_6\text{Lu}_2\text{Al}_4\text{O}_{15}:\text{Eu}^{2+}$ (circle), and $\text{Sr}_6\text{Sc}_2\text{Al}_4\text{O}_{15}:\text{Eu}^{2+}$ (diamond), normalized for brightness, plotted on a 1931 CIE diagram.

Thermal quenching

Considering the room temperature PLQY is much lower than predicted based on the structures' high calculated Θ_D , an alternative explanation for the unexpectedly low PLQY is required. The most probable cause is that the samples are thermally quenched at temperatures below 295 K. Thus, the quenching temperature (T_{50}), or the temperature at which the intensity decreases to 50% of the original intensity, was measured for all three compounds.[33-35] The emission spectra for $\text{Sr}_6M_2\text{Al}_4\text{O}_{15}:\text{Eu}^{2+}$ ($M = \text{Y, Lu, Sc}$) were collected from 80 K to 300 K in 30 K steps. At low temperature, the vibronic coupling is minimized decreasing the FWHM of the emission spectra allowing multiple Gaussian peaks from the crystallographically distinct Sr^{2+} sites to be resolved.[36] The 80 K emission data show two distinct Gaussian peaks. The peak at approximately 600 nm is most likely attributed to the site with the smallest Sr^{2+} polyhedral volume, the $[\text{Sr}(4)\text{O}_8]$. The blue shifted peak, located at 520 nm, arises from Eu^{2+} located in the three larger Sr^{2+} polyhedra with similar volumes: $[\text{Sr}(1)\text{O}_{10}]$, $[\text{Sr}(2)\text{O}_9]$, and $[\text{Sr}(3)\text{O}_{10}]$.

Figure 5. Contour plots showing the temperature dependence of the emission spectra of (a) $(\text{Sr}_{0.9975}\text{Eu}_{0.0025})_6\text{Y}_2\text{Al}_4\text{O}_{15}$ and (b) $(\text{Sr}_{0.995}\text{Eu}_{0.005})_6\text{Lu}_2\text{Al}_4\text{O}_{15}$ from 80 K to 470 K at 30 K intervals. The integrated intensity of each scan is below.

Plotting the emission spectrum as a function of temperature, as shown in Figure 5a and 5b it is evident that the measured T_{50} for both of these compounds falls well below room temperature. The yttrium analog quenches at $T_{50} = 229$ K whereas the lutetium compound has an even lower $T_{50} = 148$ K. In fact, at room temperature the intensity is less than 10% of the 80 K intensity. For $M = \text{Sc}$, the quenching was even stronger; it appears that this sample may already be quenched at 80 K based on the weak intensity measured from this sample (shown in Figure S3 of the Supporting Information). This observation follows the potential trend that T_{50} seems to decrease with decreasing M ionic radii. Unfortunately, attempts to synthesize the $M = \text{Gd}$ analogue to confirm this trend were unsuccessful.

The extreme thermal quenching can be described through two main non-radiative relaxation pathways. The first is thermally-induced photoionization where a further excitation of the electron in the $5d$ excited state to the conduction band preventing emission.[37] In the phosphor hosts investigated here, the calculated band gaps all exceed 5 eV preventing this quenching pathway from contributing to the measured behavior. The second pathway involves a phonon-assisted non-radiative relaxation to the ground state. In rare-earth substituted phosphors, the $4f$ electron undergoes a transition from the ground state (v_0) to the excited state (v_n'). The system then relaxes to its first excited state (v_0') followed, ideally, by a subsequent photon emission. However, in systems with a large shift in the excited state potential energy surface (ΔR), the relaxation process can occur non-radiatively at the crossover point by a phonon-assisted transition from the excited state to the ground state. From this analysis, it follows that thermal

quenching can be reduced by limiting ΔR and restricting the crossing point. Classically, ΔR is related to interatomic distances; thus, empirically, one might suggest the best approach to prevent a large ΔR is to develop materials that form rigid bonds.[38, 39] However, the $\text{Sr}_6\text{M}_2\text{Al}_4\text{O}_{15}:\text{Eu}^{2+}$ ($M = \text{Y, Lu, Sc}$) series of phosphors have a rigid crystal structure based on the high calculated Θ_D ; yet, these phases all show extreme thermal quenching. Thus, an alternative proxy to describe thermal quenching beyond the Debye temperature is necessary.

One potential approach is to model thermal quenching based on a phosphors Huang-Rhys factor (S). This parameter is related to the offset, ΔR , of the equilibrium position of the excited state potential energy surface following $S = \frac{1}{2}M\omega^2\Delta R^2$, where M is the reduced mass of the system.[40] In a strongly coupled (large ΔR) system $S > 5$, intermediate coupling tends to fall in the range $1 < S < 5$, and weak coupling (small ΔR) is when $S < 1$. Using the previous description of the relationship between ΔR and the thermal quenching temperature it follows that the most thermally robust system should arise in weakly coupled system. Experimentally determining the Huang-Rhys factor is often determined by fitting the temperature dependent emission spectrum.[41, 42] Although this method is useful for simple crystal structures with well-defined emission peaks, in rare-earth substituted phosphors containing multiple luminescence centers, like $\text{Sr}_6\text{M}_2\text{Al}_4\text{O}_{15}$ ($M = \text{Y, Lu, Sc}$), this model breaks down due to difficulty deconvoluting broad emission peaks into their individual components. As a result, it is not reliable to interpret the thermal quenching of the $\text{Sr}_6\text{M}_2\text{Al}_4\text{O}_{15}:\text{Eu}^{2+}$ ($M = \text{Y, Lu, Sc}$) phosphors presented using S . Instead, simple crystal structures with a range of thermal quenching temperatures that can be controlled *via* chemical substitution are needed to substantiate the relationship between thermal quenching and the Huang-Rhys factor. Once confirmed, it may be possible to discern a system's thermal quenching based on S prior to synthesis.

Conclusion

Three yellow-green phosphors, $\text{Sr}_6\text{M}_2\text{Al}_4\text{O}_{15}:\text{Eu}^{2+}$ ($M = \text{Y, Lu, Sc}$), have been synthesized using high temperature ceramic synthesis and their phase purity confirmed through high-resolution synchrotron X-ray powder diffraction. The luminescence characteristics were evaluated at room temperature when excited at 365 nm and show a much lower PLQY than expected from the computational prediction. At 80 K, these phosphors are much brighter, increasing nearly 100 times the room temperature intensity. This shows that even though Θ_D provides insight into a crystal structure's rigidity and an estimation of a compound's PLQY, it does not provide the information necessary to determine the thermal stability. An alternative model is required to reveal clues into a compound's thermal response, which in combination with the Debye temperature will comprise an essential set of tools to determine a phosphor's properties *a priori*.

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