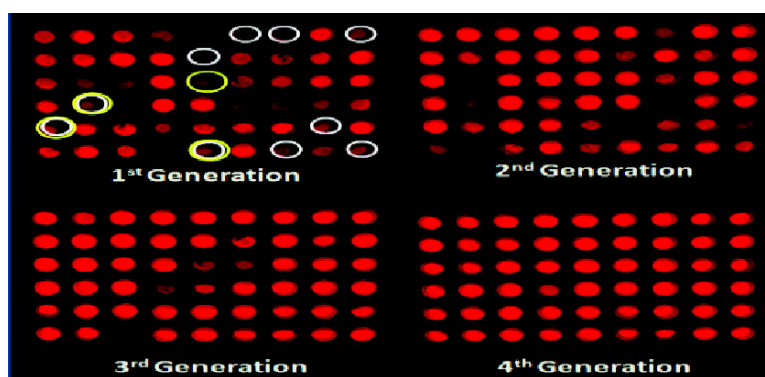


## Search for New Red Phosphors Using Genetic Algorithm-Assisted Combinatorial Chemistry

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# Search for New Red Phosphors Using Genetic Algorithm-Assisted Combinatorial Chemistry

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A genetic algorithm was employed in association with high-throughput synthesis and characterization in an attempt to search for red phosphors with high photoluminescent intensity. A tetravalent manganese-doped alkali earth germanium oxide system, with an emission color close to a desirable deep red, was screened with the assistance of a genetic algorithm to pinpoint the phosphor exhibiting the highest photoluminescence. As the genetic algorithm was in progress, the PL intensity increased and maximized in the fourth generation. The highest and the average PL intensity of the fourth generation improved by 23 and 120%, respectively, compared with that of the first generation.

## 1. Introduction

A genetic algorithm is one of the most efficient global optimization strategies and is most compatible with high-throughput combinatorial chemistry experimentation. A computational evolutionary process in association with high-throughput experimentations (so-called genetic algorithm assisted combinatorial chemistry (GACC)) has been successfully used for several years in the development of inhomogeneous catalysts and phosphors. The GACC process, used in the development of oxide-based catalysts and phosphors, has proven to be more promising in terms of searching efficiency than conventional, simple, high-throughput processes.<sup>1–9</sup>

In particular, we have recently employed GACC to develop several phosphors, the luminescent efficiency (or luminance) of which were comparable to commercially available phosphors. As a result, several tangible outcomes were obtained.<sup>8</sup> However, as the display and lighting industry converts from higher luminance to better color purity, the research direction is now focused primarily on color purity (chromaticity) and not on luminance.<sup>10–12</sup> Namely, the recent demand for actual color realization has increased and become more important. In this regard, more attention has been focused on red phosphors with high color purity.<sup>13,14</sup> This trend has led us to reconsider past phosphors, which have been forgotten because they lacked applicability to old-fashioned applications such as cathode ray tubes and gas discharge lamps. These phosphors are now being investigated on the basis of a new paradigm that we can employ in recently developed applications, such as plasma display panels, liquid crystal displays, and white light-emitting diodes. Consequently, the development and rediscovery of phosphors with better color chromaticity have become urgent in both the display and lighting industries. If the genetic

algorithm involved in the high-throughput process was employed in these industries, it would save both cost and time and increase the possibility of successful development. It is our opinion that GACC is a very efficient and practical method for researching new materials for a specific use.

The present investigation focused on using GACC to search for deep red phosphors, the color chromaticity of which should be improved compared to that of commercially available red phosphors. In fact, there are no commercially available red phosphors with the desired color chromaticity, so that the realization of a deep red color can never be achieved in the currently available displays. By employing the GACC optimization process, we aimed to identify deep red-emitting phosphors for use in a cold cathode fluorescent lamp (CCFL) that serves as a back light unit (BLU) in liquid crystal display (LCD) applications. To achieve this, a tetravalent manganese-doped alkali earth germanate system was screened by GACC in the present investigation. This system was selected on the basis of the well-known fact that tetravalent manganese-doped magnesium germanium oxy-fluoride ( $\text{Mg}_2\text{Ge}_8\text{O}_{11}\text{F}_2\text{:Mn}^{4+}$ ) was developed long ago as a deep red-emitting phosphor.<sup>15,16</sup> However, the inclusion of halides into the phosphor host structure is generally disadvantageous in both use and preparation, so new deep red-emitting oxide phosphors should be developed. Thus, we adopted the tetravalent manganese-doped system to accomplish this. Instead of excluding halides, the GACC search process was implemented so that the ratio between Mg and Ge was readjusted and simultaneously three alkali earth elements, Sr, Ca, and Ba were co-doped in an effort to search for new oxide compositions exhibiting high luminescent intensity without losing good color purity.

## 2. Experimental Procedures

The  $\text{MnO-CaO-SrO-BaO-MgO-GeO}_2$  six-dimensional library compositions were prepared and screened using a solution-dependent combinatorial library method based on

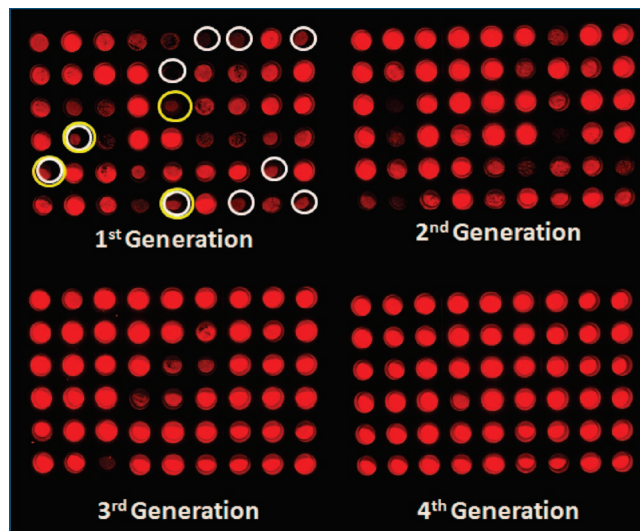
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**Table 1.** Details of the Solutions Used in Precursor Delivery

metal compd	company providing compd	solvent	solution concentration
Mn(NO <sub>3</sub> ) <sub>2</sub>	Aldrich	deionized water	0.02 M
Ca(NO <sub>3</sub> ) <sub>2</sub>	Kojundo	deionized water	0.3 M
Sr(NO <sub>3</sub> ) <sub>2</sub>	Aldrich	deionized water	0.3 M
Ba(NO <sub>3</sub> ) <sub>2</sub>	Kojundo	deionized water	0.3 M
Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Kojundo	deionized water	0.3 M
Ge-132	Aldrich	deionized hot water	0.04 M

a high-throughput screening technique. All the raw powders, such as manganese nitrate hydrous (Mn(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O), calcium nitrate hydrous (Ca(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O), strontium nitrate (Sr(NO<sub>3</sub>)<sub>2</sub>), barium nitrate (Ba(NO<sub>3</sub>)<sub>2</sub>), magnesium nitrate hydrous (Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), and Ge-132 (3,3'-(1,3-dioxo-1,3-digermoxanediyl)bispropionic acid (O[Ge(=O)CH<sub>2</sub>CH<sub>2</sub>-CO<sub>2</sub>H]<sub>2</sub>), were dissolved in deionized water. The details of the solutions used in the precursor delivery are summarized in Table 1. For the Ge solution, the organic precursor compound, commonly known as G-132, was used. At high concentrations, this compound is insoluble in water. Therefore its concentration was decreased relative to the concentration of the other solutes, and the total volume of the library was increased to 14 mL. Ge-132 is soluble in warm water; therefore, to prevent any kind of precipitation, its library was made in an ultrasonic vibronic bath at a temperature of 35 °C. The calculated volume of each solution for every generation was then pipetted into each 16 × 150 mm diameter sample test tube array, according to the composition table. For every generation, 54 samples were synthesized. The solutions were then dried at 85–100 °C for 48 h in an oven to prevent rapid evaporation and heated in a box furnace in a stepwise manner at 120 °C/4 h and 170 °C/4 h, then gently pulverized, and reheated at 500 °C/4 h. The dried samples were again pulverized and manually transferred into a specially designed alumina container called a combichem container, and they were further heated at 1150 °C for 12 h in an oxidizing atmosphere to retain manganese in the Mn<sup>4+</sup> state. This procedure was followed for all generations. After it was cooled to room temperature, a crystalline, soft, pale yellow, nonhygroscopic powder was obtained in the early generations. In the later generations, after the evolution caused by GACC, the powder turned white.

Phase identification for the best sample of each generation was performed using X-ray powder diffraction with Cu K $\alpha$  radiation at 40 kV and 30 mA (Panalytical X'pert Pro Pw 3060 MRD). The XRD patterns were obtained by normal scan (0.002°/s) measurement using a step scan mode with a step size of 0.01°. To avoid preferential particle orientation of the samples, the powder samples were mounted into a flat-plate holder using a side-filling method. For optical measurements, the emission spectrum for each generation was measured at room temperature using a laboratory-made PL instrument spectrophotometer equipped with a D2 lamp at a wavelength range 450–800 nm. All measurements were carried out in the reflection mode under an excitation of 254 nm using a continuous wave (CW) light source. The computation for the GACC optimization process was performed on a Microsoft Visual Basic platform.

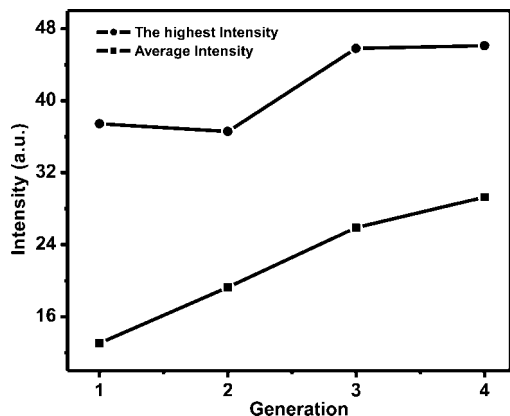


**Figure 1.** Libraries of generations first to fourth at 254 nm excitation. White and yellow circles represent Mn<sup>2+</sup> emission and melted samples, respectively.

### 3. Results and Discussion

The objective (fitness or cost) function was set as the photoluminescence (PL) intensity to be maximized in the GACC process. The PL intensity is the area under the emission spectrum of the phosphor of interest. The PL intensity was then normalized using a reference phosphor, a commercially available Y(V,P)O<sub>4</sub>:Eu<sup>3+</sup> (Samsung SDI Co. Ltd.), which is known as the best red phosphor in terms of color chromaticity. The mole fraction of six ingredient elements was set as the decision parameter in the GACC process. We introduced a restriction that the total sum of three alkali earth elements, Ca, Sr, and Ba, should not exceed 20% of Mg content, because our primary aim was to examine only the co-doping effect of the three alkali earth elements on the luminescence of a Mg-dominated system. The first generation, which contained 54 members, was randomly designed. The PL intensity was then maximized in later generations by genetic algorithm operations, such as selection, crossover, and mutation. Details regarding the GACC process adopted in the present investigation have been well-described in the literature.<sup>6–10</sup> Elitism was not a factor in our GACC process, that is, rather than preserving the promising members of the preceding generation in succeeding generations, new members were permitted to be generated in the next generation, thereby allowing for more prominent refreshment and enhanced diversity. Roulette-wheel selection was adopted and the crossover and mutation rates were set at 100% and 70%, respectively. The single-point crossover was adopted, and the crossover point was determined randomly. Mutation was achieved by addition and subtraction of an arbitrary number (referred to as the mutation number), <0.05 mol, for two arbitrarily chosen components. If the mole fraction of the chosen component was smaller than the mutation number, then the mutation number was replaced by the mole fraction of the component, such that the chosen component vanished.

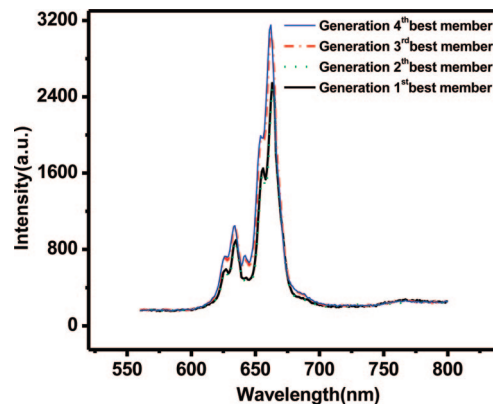
Figure 1 shows all generations produced in the GACC process from the first generation to the fourth. It is clear



**Figure 2.** Maximum and average luminance as a function of generation number.

that the two early generations included some detrimental members showing low luminescence, while in the two later generations, there were no such members. This is obviously indicative of a certain degree of evolution (or optimization) during the GACC process. There were approximately 20 unpromising members in the randomly selected first generation. The detrimental (unpromising) members were classified into three categories: melted samples, samples showing divalent, not tetravalent, manganese emission, and samples with blotches on the surface. The first and second categories were marked as yellow and white circles, and the last category (blotched samples) was conspicuous without any markings, as shown in Figure 1. It is obvious that the number of incomplete samples was reduced considerably in the second generation, such that there were neither melted nor divalent manganese samples in the second generation. Only a few blotched samples were observed in the second generation. The number of blotched samples was further reduced in the third generation and eventually vanished in the fourth generation. The evolution of sample appearance was obvious in our GACC process, even though our objective function was luminescent intensity, regardless of whether blotches formed. This finding would lead to the conclusion that the GACC process was executed effectively. Consequently, it is apparent that the blotched appearance of the sample gave rise to the lower luminescent intensity. It is not surprising, then, to see that the evolution of some properties had a direct correlation with the objective function of interest. It is worth noting that both the luminescent intensity and the powder condition improved significantly after only four generations of the GACC process.

The average and maximum intensity of each generation was plotted as a function of the generation number, as shown in Figure 2. The average intensity increased by more than 120% up to the fourth generation. The maximum intensity also increased by 23% from the first generation to the fourth even though the second generation showed a slight decrease. Such a slight drop in fitness, which was only about 2%, can be ignored. This drop in fitness has been faced frequently in experimental error-involved processes and was detected in our previous GACC executions.<sup>8</sup> Figure 3 shows the emission spectra of the best members of each generation. The emission peak distribution was identical, regardless of the phosphor composition. The narrow bands constituting



**Figure 3.** Emission spectrum of the best members of each generation.

**Table 2.** Compositions of the Best Members along with EDS Data from the First to the Fourth Generation<sup>a</sup>

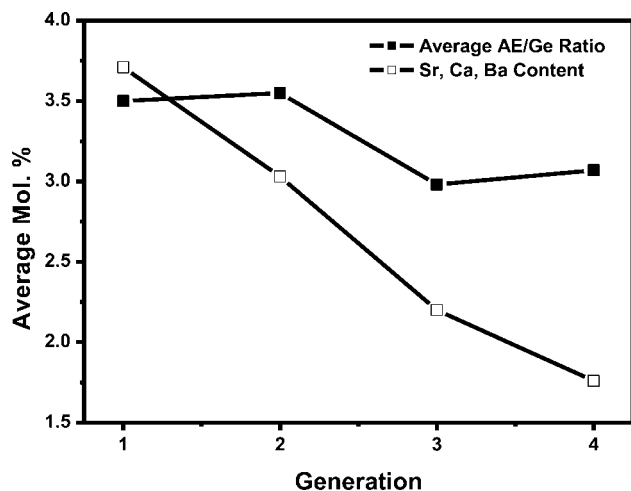
	Sr	Ca	Ba	Mg	Ge	Mn
generation 1	<b>3.60</b>	<b>1.35</b>	<b>1.04</b>	<b>68.93</b>	<b>24.97</b>	<b>0.11</b>
EDS	0.72	0.60	0.37	75.31	22.89	0.12
	1.01	0.71	0.51	72.84	24.88	0.05
	4.04	0.99	1.26	70.77	22.83	0.12
generation 2	<b>6.03</b>	<b>1.81</b>	<b>0.00</b>	<b>67.93</b>	<b>23.89</b>	<b>0.33</b>
EDS	4.35	1.08	0.00	73.49	20.81	0.27
	2.75	0.76	0.00	70.65	25.62	0.21
	1.68	0.78	0.00	73.64	23.77	0.13
generation 3	<b>0.85</b>	<b>0.66</b>	<b>0.00</b>	<b>73.94</b>	<b>24.23</b>	<b>0.33</b>
EDS	0.43	0.15	0.00	75.19	23.99	0.25
	0.28	0.43	0.00	70.51	28.64	0.14
	0.52	0.40	0.00	78.23	20.58	0.27
generation 4	<b>0.00</b>	<b>0.69</b>	<b>0.00</b>	<b>74.55</b>	<b>24.43</b>	<b>0.33</b>
EDS	0.14	0.40	0.00	79.05	20.13	0.28
	0.18	0.48	0.00	74.04	25.04	0.27
	0.16	0.61	0.00	77.79	21.14	0.31

<sup>a</sup> Oxygen content was excluded from the table for convenience.

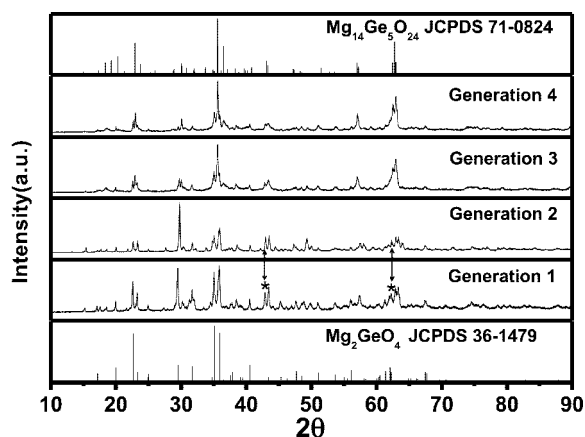
the emission spectra originated from the Jahn–Teller splitting of  ${}^4F_2 \rightarrow {}^4A_2$  transitions of  $Mn^{4+}$  ( $d^3$ ) ions.<sup>15</sup>

Table 2 exhibits the composition values of the best members along with the results from the elemental analysis using energy-dispersive spectroscopy (EDS) from the first to fourth generation. The EDS result was in a relatively good agreement with the processing compositions within an acceptable experimental error range. EDS analysis is powerful for a rough measure of composition, but it is not 100% correct. However, the coincidence between the processing composition and the EDS result reflects that our elemental control was in good order. A table exhibiting the entire compositions sorted by their fitness (luminescent intensity) in descending order is presented in the Supporting Information. We examined two practical and important factors, that is, the ratio of the entire alkali earth content (Mg, Sr, Ca, Ba) to the Ge content (AE/Ge), and the total amount of Sr, Ca, and Ba co-dopants, which were thought of as a substituent for Mg. The average AE/Ge ratio and the sum of Sr, Ca, and Ba of the top five members of each generation were plotted as a function of the generation number in Figure 4. The AE/Ge ratio increased slightly and then approached the value of the best member of the fourth generation. The total content of Sr, Ca, and Ba decreased dramatically in later generations, suggesting that the addition of these three alkali earth substituent elements played no role in enhancing luminescent intensity. In fact, the composition of the best





**Figure 4.** AE/Ge ratio and mole fraction of Sr, Ca, and Ba of top five members as a function of generation number.



**Figure 5.** XRD patterns of the best samples obtained from each generation. The exact composition is presented in Table 2.

sample in the later (third and fourth) generations contained very small amounts of these alkali earth co-dopants, enough to be neglected. It is noteworthy that the elimination of Sr, Ca, and Ba co-dopants resulted from the evolution process to which GACC gave rise.

We did not produce further generations, but stopped the GACC process at the fourth generation because the unpromising members had been eliminated and the variance of the overall intensity level was small in the fourth generation. More importantly, no further improvement was intuitively expected thereafter. Rather than producing more generations, our attention was focused on the identification of promising members found at the current stage. The best members of each generation, the exact composition of which was presented in the top row of every generation in Table 2, were examined by X-ray diffraction (XRD). The XRD patterns are presented in Figure 5 together with two standards from the Joint Committee on Powder Diffraction Standards (JCPDS). The best members of the first and second generation consisted mainly of  $\text{Mg}_2\text{GeO}_4$ . Weak traces of  $\text{Mg}_{14}\text{Ge}_5\text{O}_{24}$  were also detected in the best members of the first and second generations. In particular, the presence of a starting material,  $\text{MgO}$ , was also observed as an undesirable impurity, which might have been detrimental to luminescence. On the other hand, the phase identification for the best members of the two later genera-

tions yielded quite different features. Namely,  $\text{Mg}_{14}\text{Ge}_5\text{O}_{24}$  became a main phase, and a portion of  $\text{Mg}_2\text{GeO}_4$  was minimized. More importantly, there remained no undesirable impurity originating from the starting materials. The computational GACC process gave rise to the evolution from  $\text{Mg}_2\text{GeO}_4$  to  $\text{Mg}_{14}\text{Ge}_5\text{O}_{24}$  and allowed for the elimination of  $\text{MgO}$ . The actual, exact stoichiometry of the main phase constituting the best sample in the fourth generation was proven to be  $\text{Mg}_{14}\text{Ge}_5\text{O}_{24}$ . The initial processing composition was in a good agreement with this stoichiometry as was evidenced in Table 2. It is manifest that the elemental control in our GACC process was in good order. To back up this, we separately synthesized  $\text{Mg}_{14}\text{Ge}_5\text{O}_{24}:\text{Mn}^{4+}$  by adopting starting compositions without any AE co-dopants. Similar luminescence from tetravalent manganese emission also was observed in this auxiliary test, as in the previous GACC result.

It should be noted that the structures of  $\text{Mg}_{14}\text{Ge}_5\text{O}_{24}$  compounds are well-known,<sup>17</sup> and several similar compounds incorporating divalent manganese were once considered to be red phosphors.<sup>18</sup> However, tetravalent manganese-activated  $\text{Mg}_{14}\text{Ge}_5\text{O}_{24}$  systems have never been considered as phosphors. Even though they do not have efficient emission in comparison to halide-involved magnesium germanate systems such as  $\text{Mg}_2\text{Ge}_8\text{O}_{11}\text{F}_2:\text{Mn}^{4+}$ , the color chromaticity of  $\text{Mg}_{14}\text{Ge}_5\text{O}_{24}:\text{Mn}^{4+}$  phosphors (CIE  $x = 0.71$ , CIE  $y = 0.29$ ) is as good as that of the  $\text{Mg}_2\text{Ge}_8\text{O}_{11}\text{F}_2:\text{Mn}^{4+}$  phosphor. More importantly, it is worth emphasizing that GACC enabled the reproducible production of  $\text{Mg}_{14}\text{Ge}_5\text{O}_{24}:\text{Mn}^{4+}$  phosphors. As already mentioned in the introduction section, the major goal of the present GACC is not to find a completely new compound but to endow well-known compounds with a new functionality in relation to newly developed applications and, in addition, to optimize and fine-tune the composition to maximize the property of interest. In this regard, GACC is an excellent tool for either the development of new phosphors or the rediscovery of required applicability from well-known compound systems. More importantly, GACC enabled us to complete the design of experiments with high precision and reliable reproducibility in a very short time frame. The GACC approach adopted in the present investigation revealed that  $\text{Mg}_{14}\text{Ge}_5\text{O}_{24}:\text{Mn}^{4+}$  has promise as a deep red phosphor for CCFLs in LCDs.

#### 4. Conclusion

The GACC optimization process was employed to search for deep red phosphors by screening tetravalent manganese-doped alkali earth germanium oxide systems, in an attempt to use them in flat panel displays or lighting systems. The GACC process significantly facilitated the search process.

Four generations, including 216 phosphor samples, were produced by the GACC process. The maximum and average luminescent intensity was improved by 23% and 120%, respectively, during the GACC process. Phase identification using XRD of promising samples resulting from the GACC process revealed that the sample with maximum luminescent intensity consisted of a main phase,  $\text{Mg}_{14}\text{Ge}_5\text{O}_{24}:\text{Mn}^{4+}$ , and a minor phase,  $\text{Mg}_2\text{GeO}_4:\text{Mn}^{4+}$ . Whereas the luminescent

intensity of our best sample still needs more improvement, its color chromaticity is better than that of any other commercially available red phosphors. Consequently, it might be possible to use this deep red phosphor in either flat panel displays or in white-light-emitting diodes. This process could be aided if the luminescence were enhanced slightly by optimization of some of the extrinsic properties, such as powder size and shape, which were not considered in the present investigation.

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**Supporting Information Available.** A table exhibiting the entire compositions sorted by their fitness (luminescent intensity) in descending order. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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