

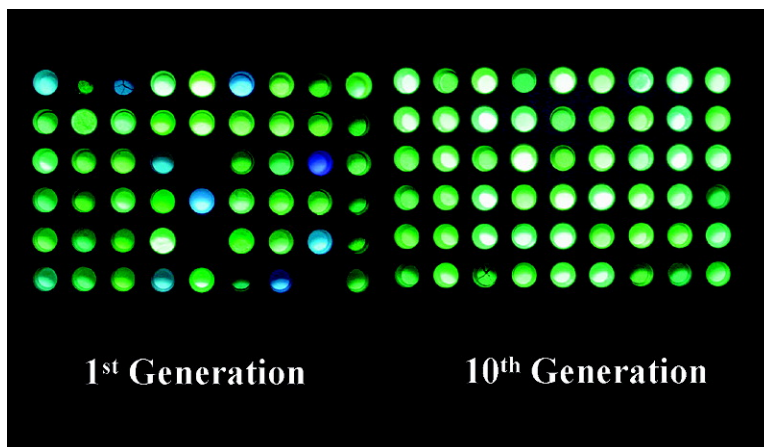
Article

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Genetic Algorithm–Assisted Combinatorial Search for a New Green Phosphor for Use in Tricolor White LEDs

Kee-Sun Sohn,* Duk Hyun Park, Sang Ho Cho, Byung Il Kim, and Seong Ihl Woo†

Department of Materials Science and Metallurgical Engineering, Suncheon National University, Chonam 540-742, Korea, and Department of Chemical and Biomolecular Engineering & Center for Ultramicrochemical Process Systems, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea

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An evolutionary optimization process involving a genetic algorithm and combinatorial chemistry was employed for the development of green phosphors which are suitable for tricolor white-light-emitting diodes. To accomplish a high luminescent efficiency at 400 nm excitation, we screened a seven-cation oxide system including Tb, Gd, Ce, Mg, Si, Al, and B. The combination of a genetic algorithm and combinatorial chemistry enhanced the searching efficiency when applied for phosphor screening. As a result, the optimized composition was $\text{Tb}_{0.01}\text{Gd}_{0.02}\text{Ce}_{0.04}\text{B}_{0.1}\text{Si}_{0.83}\text{O}_8$. The luminance of this borosilicate glass was 67% that of ZnS:Cu,Al at 400-nm excitation.

Introduction

White-light-emitting diodes (LEDs) have attracted interest because of the possibility of their being used as general lighting devices. The combination of blue chip and yellow phosphor has already been developed for realizing white light, but a tricolor white LED consisting of a soft-UV chip and RGB phosphors is still challenging.^{1–3} For the tricolor white LEDs developed so far, InGaN chips have been under consideration as excitation sources for RGB phosphors. In this case, inorganic oxides would be the best candidates for the RGB phosphors for three-band white LEDs, even though their luminescence efficiency is inferior to either organic dyes or other inorganic phosphors, such as sulfides.^{1–3} It should, however, be noted that the lifetime of organic materials is too short and that sulfide phosphors under consideration pose some problems in use because sulfur tends to soak into InGaN chips and gives rise to the ensuing erosion. To avoid such problems, our objective was to develop new oxide-based RGB phosphors. A red oxide phosphor has been developed by employing an evolutionary optimization strategy in our previous investigation.⁴ The structure of this new red phosphor has been proven to be oxyapatite.⁵ In addition, Neeraj et al. also found promising oxide red phosphors for tricolor white LEDs, which are in scheelite and westfieldite structures.^{6,7}

Turning our attention to green phosphors in the present investigation, the evolutionary optimization methodology that we had adopted in our previous work⁴ was also employed to search for new green phosphors based on a Tb^{3+} activated oxide system, including such cations as Gd, Ce, Mg, Si, Al, and B. Namely, genetic algorithm–assisted combinatorial chemistry (GACC) was employed to develop new green phosphors for tricolor white LEDs. The seven elements that

we adopted were chosen by analyzing the composition of existing oxide green phosphors that have been developed to date for use in various applications such as fluorescent lamps, cathode ray tubes, vacuum fluorescent display, plasma display panels, field emission displays, etc. There could be a large number of stoichiometric compounds (single-phase line compounds) along with a huge number of their solid solutions and also an infinite number of glassy compositions in this seven-dimensional composition system. No matter how many kinds of structure exist in this seven-dimensional composition parameter space, we need to screen the photoluminescence property and pinpoint potential candidates. As already mentioned, however, the number of samples would be too huge to screen them, even if we employed the conventional combinatorial chemistry. Heuristics such as a genetic algorithm is powerful to sort out such a complication that comes from the abundance of candidates to be screened.

The GACC approach has recently attracted interest due to its ability to compensate for the weak points in the traditional high-throughput combinatorial chemistry in the pharmaceutical research area.^{8–10} When the area of inorganic material synthesis and screening is combined with GACC, it has recently been used for the development of heterogeneous catalytic materials.^{11–13} As a result, the GACC approach has been found to be very efficient and promising in a search for new inorganic catalytic materials. More importantly, we have employed this strategy to develop inorganic phosphor materials for the first time.⁴ It is our opinion that inorganic phosphors are more suitable for the GACC method on the basis of the fact that the screening process can be greatly facilitated, as compared to that for catalytic materials. We have constructed a solution-based combinatorial chemistry method that allows a 54-composition library (per generation) to be completed in only 2 or 3 days.^{14–20} Our solution combinatorial chemistry system of a

* Corresponding author. E-mail: kssohn@sunchon.ac.kr.

† Korea Advanced Institute of Science and Technology.

relatively small library (only 54 compositions are available per each generation) is not comparable to a thin-film or ink-jet printing combinatorial chemistry system consisting of thousands of compositions in view of screening efficiency.^{21–23} However, the introduction of the genetic algorithm to our small library solution combinatorial chemistry system made it possible to augment the efficiency.

Experimental Procedures

The overall process of the combinatorial chemistry system adopted in the present investigation is described in more detail in our previous reports.^{14–20} The Gd and Si solutions were prepared by dissolving Gd₂O₃ and Si(C₂H₅O)₄ (TEOS) in nitric acid. The Tb, Mg, Ce, Al, and B solutions were prepared by dissolving Tb(NO₃)₂·6H₂O, Mg(NO₃)₂·6H₂O, Ce(NO₃)₂, Al(NO₃)₃, and H₃BO₃ in deionized water. The correct amount of each solution was then injected into a 6-mL test tube array according to the library design. The solutions in the tubes were dried at 80 °C for 24 h. These samples were further dried at 600 °C for 2 h. The dried samples were pulverized and collected in a specially designed ceramic container (given the name combi-chem container or library plate) and subsequently fired at 900 °C for 2 h in a neutral atmosphere of N₂ gas.

The emission spectra were monitored at 400 nm, which simulates an InGaN LED light source, with the samples being left in the combi-chem containers in a high-throughput manner using a plate reader accessory attached to a Perkin-Elmer LS50B spectrometer with a xenon flash lamp. The luminance was calculated by integrating the product of the emission spectrum and the standard visual spectral efficiency curve on the basis of CIE regulation.²⁴ Some of the samples chosen among the library were removed from the combi-chem containers and examined by X-ray diffraction (XRD).

GACC. The GACC begins with 54 random compositions. This randomly chosen library is called “the first generation”. As a matter of fact, the first generation was not thoroughly random. We introduced a lot of zeros to reduce the composition dimensionality. Even though some others have separated the composition code into existence and composition codes for this sake,¹³ we simply introduced ~10 to 20% of zeros for each element. Evolutionary operations such as elitism, selection, crossover, and mutation were then applied to this first generation using the actually measured luminance values of all the members in the first generation. This computational evolutionary process yielded another new library, which is called the second generation, having the same number of compositions as the first one. The second generation showed a somewhat improved luminance. The same processing was done on the second generation and yielded the third generation, and so on. This process will improve the luminance of all the members in the generation as the generation number increases, finally leading us to the optimum. Namely, the GACC includes repetitions of the experiment, including synthesis and luminance measurement and the computational evolutionary operation, on the basis of the measurement results. It can be thus summarized that the GACC consists of two parts: one is the experimental part and the other is the intermediate computational part.

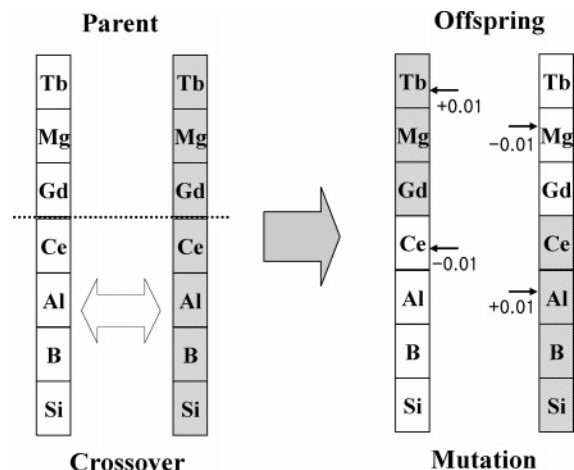


Figure 1. Schematic description of crossover and mutation in the genetic algorithm used for both simulation and experiment. The crossover and mutation positions were determined randomly.

The selection, crossover, and mutation rates were all set at 100%. The roulette wheel selection was adopted. The simple principle of roulette wheel selection is that the higher the luminance, the higher the opportunity of being selected. Nonetheless, it does not mean that only the high luminance members have an opportunity of being selected. It should be noted that some members of low luminance level could give a refreshing effect occasionally. Elitism was also involved, that is, the two highest compositions in the former generation were elicited and copied to the next generation. Elitism plays a significant role not only in preserving the excellence but also in checking the experimental consistency in the case of experimental evolutionally processes. Namely, by incorporating the copied members into the next generation, they could act as an effective indicator to examine the consistency of the synthesis process of each generation. The single-point crossover was adopted, and the crossover point was determined randomly. The composition was normalized after the crossover. The mutation was achieved by adding and subtracting a random number for two arbitrarily chosen components, respectively. The operation of crossover and mutation are described schematically in Figure 1. Two parent members chosen by the roulette wheel selection method were represented as composition bands, as can be seen in Figure 1. One of them was shaded to discriminate between them and, hence, to trace them out after the crossover. They were treated as chromosomes, and the element sectors were regarded as genes that have some information affecting the luminance of the member. The crossover created two offspring by exchanging the genes of the parents, and the subsequent mutational operation was executed on these offspring.

The population size adopted for the experimental optimization process was 54. Considering the simulation result that the optimization efficiency is not affected significantly by the population size if it exceeds 50,⁵ it would be favorable for the population size to be as small as possible from a practical point of view, that is, the population size (54) is good enough for complete optimization, even though we have adopted a larger population size (108) in our previous report.⁴

Results and Discussion

Table 1 shows the compositions and their corresponding luminance of 10 libraries (generations). The whole population (54 random compositions) in the first generation was listed in the order of decreasing luminance; however, only the top 11 members, which is ~20% of the whole population, were included in the other generations from the second to the tenth. Two members copied to the next generation by elitism were marked by the bold font. There was no significant difference in luminance of these copied members between former and later generations throughout the whole process, which validates the consistency of our experimental system involving high-throughput synthesis and characterization. When scrutinizing the trend of compositional change shown in Table 1, it is obvious that the evolution of the top eleven compositions took place in two directions in the early stages, and then one of these directions became predominant and the other perished. That is, magnesium-rich members were observed until the sixth generation, but they disappeared after that. The highest luminance was saturated in the sixth generation. The composition of the highest luminance was approximated to $\text{Tb}_{0.01}\text{Gd}_{0.02}\text{Ce}_{0.04}\text{B}_{0.1}\text{Si}_{0.83}\text{O}_8$, which is denoted as sample S, and this optimum composition did not change after the sixth generation due to elitism. In fact, the exact composition of sample S is shown in Table 1, which was rounded off to the above simplified notation just for compactness.

Figure 2 shows the average mole fraction of each component for the top 11 compositions for each generation. The GACC weeded out useless elements automatically by the evolutionary principle. In fact, such a weeding out process actually took place in the present investigation. Namely, even though we started with a seven-element system, magnesium and aluminum were rapidly weeded out. The top 11 compositions do not deviate greatly from the composition of the highest luminance in later generations after the eighth generation, as can be seen in Table 1. This proved that the evolutionary optimization certainly took place during our experimental process. It should be noted that if the optimization were completed, the composition of almost all the members in a certain generation would converge approximately to the vicinity of a global optimum point but should never be identical. However, we could never be met with such a situation in the actual optimization process, including experimental parts, but the composition of several high-ranking members in relatively later generations could get closer to a certain composition. This type of convergence propensity at later iterations is a nature of the genetic algorithm. Consequently, it is reasonable to take into account the average composition of the top 11 members in Figure 2 rather than the composition of only the best member.

Figure 3 shows the photographs of the first and tenth generations taken under an excitation of 365 nm. The lamp light was illuminated evenly over the library, so that we can see a relative comparison. Even though the excitation light wavelength of the lamp (365 nm) differs from the 400-nm excitation that was adopted for quantitative measurements, it is clear that the tenth generation contains many more promising compositions in terms of luminance than the first. Figure 4 shows the quantitative results, in which the highest

and average luminance values of each generation are plotted as a function of generation number. As can be seen in Figure 4, both values increase with increasing generation number, and the maximum luminance began to saturate at the sixth generation. Consequently, the composition of the highest luminance was fixed at a composition after that. Such a saturated propensity was ascribed to elitism. Every generation contained a considerable number of glassy members. In contrast to our previous report,⁴ in which glassy members had all been precluded prior to the computation by setting their luminance values at 0, irrespective of the intensity of their luminescence, thereby reducing the number of glassy members in the next generation, we allowed for all the glassy members in the present investigation. As a result, there were a large number of glassy members in the tenth generation, which means that the evolutionary process took place by relying on only the luminance itself, not on whether it was a crystalline or glassy phase. By considering the fact that the highest luminescence is not always elicited from crystalline compounds, a glassy phase would be also better suited to the host of Tb^{3+} emission. In fact, glassy members exhibited more promising luminance than crystalline members in the present case.

From a practical point of view, it is more important to investigate how promising the luminance level of sample S is and to identify the constituent phases by structural analysis. By doing so, we could achieve our final goal, which is to secure the reproducibility of sample S by the conventional solid-state reaction method. Figure 5 shows the emission spectra of sample S, along with the best member in the first generation and a commercially available sulfide phosphor for comparison. The luminance of sample S was much higher than the best member in the first generation. The luminance was enhanced by ~6 times during the GACC process. This means that a considerable evolution arose during the GACC process. Such a huge improvement has never been reported before in both cases of phosphors and catalysts.^{4,11–13} Even though this may be a result of relatively low luminance in the starting generation, it still seems exciting to us to see the GACC working properly. When compared to a commercially available $\text{ZnS}:\text{Cu},\text{Al}$ green phosphor, the luminance of sample S reaches ~67% of that of $\text{ZnS}:\text{Cu},\text{Al}$ green phosphor. Consequently, even though sample S is inferior to sulfide phosphors in terms of luminance, it could be more suitable for tricolor white LEDs by evoking the erosive nature of sulfide phosphors at high temperatures.

It is worthwhile to identify the structure of sample S by the XRD analysis. In contrast to the previous case in which we had obtained a well-developed single-phase crystalline structure by GACC,⁵ we did not find any crystalline phases among the members that exhibit relatively high luminance in the tenth generation. It is thus concluded that sample S did not crystallize into well-ordered structure, but instead formed a glassy phase. All other members that exhibit relatively high luminance in the tenth generation were also proven to be borosilicate or silicate glasses, but they were not in melted form, and they looked like glittering powder judged by externals. Therefore, there are no particular issues to be discussed in conjunction with structural analysis. That

Table 1 (Continued)

Tb	Gd	Ce	Mg	Si	Al	B	luminance	Tb	Gd	Ce	Mg	Si	Al	B	luminance
8th Generation															
0.010	0.020	0.038	0.000	0.830	0.000	0.098	195.980	0.008	0.000	0.047	0.000	0.881	0.000	0.053	118.740
0.009	0.000	0.047	0.000	0.878	0.000	0.055	148.480	0.010	0.000	0.038	0.012	0.874	0.000	0.056	114.360
0.012	0.017	0.035	0.000	0.878	0.000	0.055	137.740	0.022	0.000	0.034	0.000	0.852	0.024	0.059	104.190
0.020	0.000	0.037	0.000	0.877	0.000	0.055	137.520	0.010	0.000	0.047	0.000	0.883	0.020	0.030	103.590
0.010	0.000	0.047	0.000	0.878	0.011	0.045	136.730	0.008	0.000	0.045	0.000	0.880	0.000	0.054	102.760
0.008	0.000	0.037	0.000	0.888	0.000	0.055	127.990								
9th Generation															
0.010	0.020	0.038	0.000	0.830	0.000	0.098	197.080	0.010	0.020	0.028	0.012	0.867	0.000	0.054	139.080
0.011	0.020	0.036	0.000	0.882	0.000	0.059	146.920	0.008	0.000	0.037	0.012	0.886	0.010	0.038	157.870
0.020	0.000	0.034	0.000	0.862	0.014	0.059	146.840	0.020	0.000	0.036	0.012	0.858	0.010	0.055	137.520
0.009	0.000	0.045	0.000	0.825	0.010	0.101	142.650	0.010	0.020	0.038	0.012	0.866	0.000	0.054	135.430
0.009	0.000	0.047	0.000	0.878	0.000	0.055	140.250	0.020	0.000	0.036	0.000	0.872	0.020	0.042	133.610
0.010	0.000	0.038	0.012	0.885	0.000	0.046	140.030								
10th Generation															
0.010	0.020	0.038	0.000	0.830	0.000	0.098	198.890	0.012	0.017	0.044	0.000	0.826	0.000	0.090	135.510
0.010	0.020	0.027	0.011	0.882	0.000	0.048	152.550	0.019	0.000	0.035	0.012	0.861	0.020	0.044	131.570
0.010	0.000	0.047	0.012	0.870	0.000	0.052	151.550	0.008	0.000	0.037	0.011	0.880	0.020	0.034	129.600
0.019	0.000	0.036	0.012	0.859	0.020	0.045	144.230	0.022	0.000	0.045	0.000	0.865	0.000	0.059	129.360
0.020	0.000	0.036	0.012	0.868	0.011	0.045	141.060	0.010	0.000	0.040	0.000	0.742	0.038	0.160	126.840
0.011	0.020	0.036	0.000	0.882	0.000	0.059	137.570								

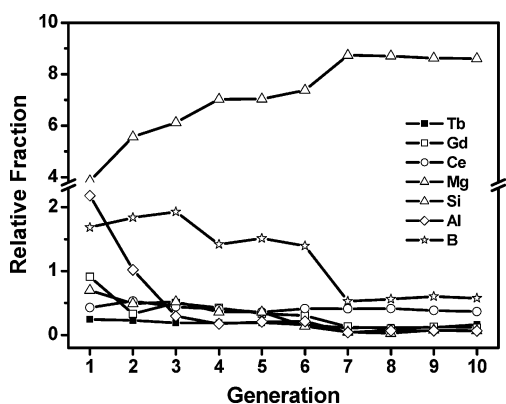


Figure 2. Average mole fraction of each component for the top 11 compositions of each generation.

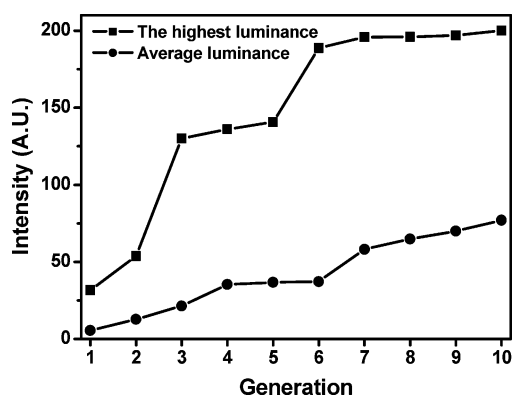


Figure 4. Maximum and average luminance as a function of generation number.

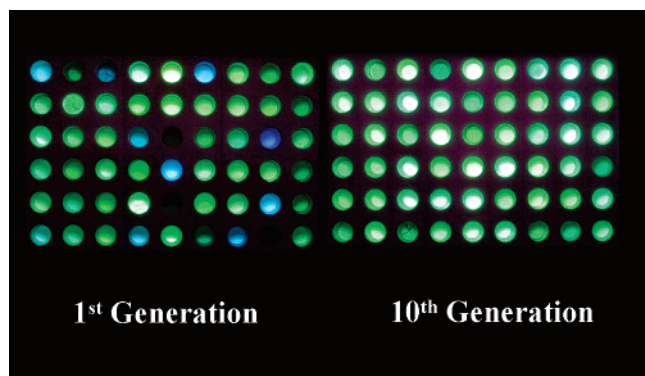
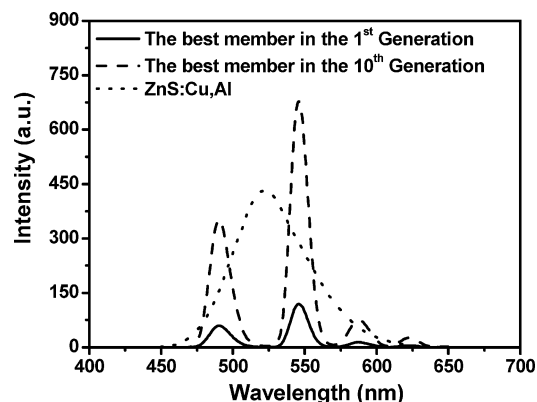


Figure 3. Libraries of both the first and tenth generations at 365-nm excitation. A considerable improvement was obtained in the tenth generation.

is why we did not present any XRD data here. It is also presumed that a small amount of elements such as Gd and Ce could act as sensitizers to help the absorbed energy transfer to the activator (Tb^{3+} ions in this case). In fact, these two elements have been very well-known as a sensitizer and also known to form absorption bands in the soft ultraviolet range.²⁵

Glass phosphors (or luminescent element-doped glasses) have never been used in actual applications in relation to

Figure 5. Emission spectra of $Tb_{0.01}Gd_{0.02}Ce_{0.04}B_{0.1}Si_{0.83}O_{\delta}$, the best member in the first generation, and commercially available ZnS:Cu,Al phosphors for comparison.

displays and lightings, despite the fact that they have been used as light amplifiers in light telecommunication systems and that they have also been useful for theoretical investigations on the energy level of rare earth ions. However, glass phosphors recently began to attract interest as the luminescence efficiency has been improved in the visual range.²⁶ Accordingly, it is suggested that our glass phosphor should be applied for tricolor white LEDs, even though we cannot

find any precedents and the current luminance level needs further improvement.

Conclusions

In summary, the GACC process made it possible to facilitate the search process for a new oxide-based green phosphor for use in tricolor LEDs. The maximum and average luminance increased with the generation number and, in particular, the maximum luminance was saturated only six generations after the onset of the GACC process. In addition, the maximum luminance that was obtained in the sixth generation was six times as high as the luminance of the best member in the first generation. The composition of the maximum luminance was determined to be $Tb_{0.01}Gd_{0.02}Ce_{0.04}B_{0.1}Si_{0.83}O_{\delta}$ (sample S). As a result of phase identification, this optimum composition was proven to be a glassy phase. The luminance of sample S was 67% of that of well-known ZnS:Cu,Al green phosphor at 400-nm excitation. Consequently, it could be possible to adopt this new phosphor as a green phosphor for tricolor white LED applications if the luminance is enhanced slightly by optimizing some extrinsic properties, such as powder size and shape.

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