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Computational Evolutionary Optimization of Red Phosphor for Use in Tricolor White LEDs

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An evolutionary optimization process involving a genetic algorithm and combinatorial chemistry was employed in an attempt to develop titanate-based red phosphors suitable for use in tricolor white light-emitting diodes. An eight-cation oxide system, including $(K,Li,Na)_x(Y,Gd,La,Eu)_yTi_zO_\delta$, was screened in terms of luminescence efficiency. The use of a combination of a genetic algorithm and combinatorial chemistry enhanced the efficiency of searching, as it is applied to the screening of phosphors in a limited composition space. As a result, the optimum composition was determined to be $(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO_4{:}Eu^{3+}$, the reproducibility of which was achieved by the conventional solid-state reaction method. Using the $(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO_4{:}Eu^{3+}$ phosphor and an InGaN chip, a red LED was realized, so that the applicability of this new phosphor to white LEDs was confirmed. The luminescence of this phosphor was 110% that of the well-known scheelite variant phosphor and 600% that of a commercially available $Y_2O_2S{:}Eu^{3+}$ at an excitation of 400 nm.

Introduction

White light-emitting diodes (LEDs) are considered to be good general lighting devices. Their substitution for fluorescence or incandescence lamps would lead to considerable energy savings. The combination of blue chip and yellow phosphors has already been developed and is commercially available, but tricolor white LEDs consisting of a soft UV chip emitting at a 400 nm wavelength with red, green, and blue (RGB) phosphors continues to be a challenge.[1−3] In the case of the tricolor white LED, inorganic oxides would be the best candidates for RGB phosphors in terms of both chemical stability and luminescence efficiency. However, promising red oxide phosphors have not yet been found, although some good candidates for green and blue phosphors have been developed. Thus, the development of a good red phosphor is a key technology for achieving a tricolor white LED lighting system. In this regard, we developed a red phosphor with an oxyapatite structure by employing an evolutionary optimization strategy.[4−6] In addition, Neeraj et al. found more promising oxide red phosphors for tricolor white LEDs, which are in scheelite and westfieldite structures.[7,8] A scheelite variant red phosphor has proven to be the best among those developed to date. However, more-efficient red phosphors are needed to achieve an acceptable efficiency of white LED. In this regard, a new, smart strategy for developing better red phosphors is needed. The genetic algorithm, assisted combinatorial chemistry (GACC), which combines a computational evolutionary optimization strategy with high-throughput synthesis and characterization processes, was employed to develop new red phosphors for tricolor white LEDs. Our goal was to develop a new red phosphor, the luminescence efficiency of which should exceed that of the scheelite variant phosphor. To achieve this, we screened and optimized an alkali metal lanthanide titanate system ($(K,Li,Na)_x(Y,Gd,La,Eu)_yTi_zO_\delta$) by the GACC process.

The GACC approach has recently attracted interest because of its ability to compensate for the weak points in the traditional high-throughput combinatorial chemistry in the pharmaceutical research area.[9−11] Inorganic material synthesis and screening, in association with GACC, has recently been used for the development of heterogeneous catalysts.[12−14] As a result, the GACC approach was found to be very efficient and promising in searching for heterogeneous catalysts on

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Table 1. Details about the Solutions Used in Precursor Delivery

metal compd	company providing compd	other additives to solution	metal concentration
Li_2CO_3	Aldrich	2% HNO_3	0.5 M
Na_2CO_3	Kojundo	deionized water	0.5 M
K_2CO_3	Kojundo	deionized water	0.5 M
Y_2O_3	Kojundo	8% HNO_3	0.5 M
Gd_2O_3	Kojundo	10% HNO_3	0.5 M
$Ti(OC_2H_5)_4$	Aldrich	ethanol	0.5 M
Eu_2O_3	Kojundo	11% HNO_3	0.5 M

the basis of an inorganic oxide system. More importantly, inorganic phosphors are more suitable for the GACC method, because the screening process can be greatly facilitated relative to that for catalysts. In this regard, we employed this strategy to develop inorganic phosphor materials for the first time.[4,6] According to our previous report on red phosphors for tricolor white LEDs,[4,5] the evolutionary process identified a well-crystallized single phase (oxyapatite) in the sixth generation. Unfortunately, even though we confirmed the effectiveness of GACC for the development of phosphors, the final product was not practically useful. In the present investigation, however, the aim was to develop promising new red phosphors, the luminescence property of which would be acceptable from the practical point of view, so that they can be quickly used in actual applications.

Experimental Procedures

Na and K solutions were prepared by dissolving Na_2CO_3 (99.9%) and K_2CO_3 (99.9%) in deionized water. Li, Y, Gd, La, and Eu solutions were prepared by dissolving Li_2CO_3, Y_2O_3, Gd_2O_3, La_2O_3, and Eu_2O_3 (all 99.99%) in nitric acid. The Ti solution was prepared by dissolving $Ti(OC_2H_5)_4$ (99.99%) in ethanol. The details about the solutions used in the precursor delivery are summarized in Table 1. The correct amount of each solution was then injected into a 6 mL test tube array according to the library design. This solution preparation and dispensing process was done inside the glovebox. The solutions in the tubes were agitated in an ultrasonic bath for 2 h and then dried at 80 °C for 24 h. Most of the solutions turned into gel states at this stage and were further dried at 100 °C for 24 h. These samples were heat treated at 500 °C for 3 h for complete drying. The dried samples were pulverized and collected in a specially designed container made of alumina ceramic (given the name combi-chem container or library plate) and successively fired in a three-step process, i.e., at 700 °C for 3 h, 900 °C for 2 h, and finally 1100 °C for 2 h, in an ambient atmosphere. Intermediate pulverizations were also done during the three-step process.

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. Luminescence was calculated by integrating the product of the emission spectrum and the standard visual spectral efficiency curve on the basis of CIE regulations.[24] Some of the samples chosen among the library were removed from the combi-chem containers and examined by X-ray diffraction (XRD).

Computational Process

Evolutionary optimization was implemented in the multicomposition $A_xR_yTi_zO_\delta$ (A= K, Li, Na; R= Y, Gd, La, Eu) system. There are a large potential number of stoichiometric compounds (single-phase line compounds) along with a huge number of solid solutions and mixtures there of in this eight-dimensional composition system. Unlike our previous study, in which completely random compositions were treated,[4,6] the fundamental stoichiometry x, y, and z was not thoroughly random but set as several combinations of simple integers, which were elicited from well-known databases such as the inorganic crystal structure database (ICSD) and the joint committee for powder diffraction standards (JCPDS). As a result, the parameter space could be significantly reduced, which enhanced the searching efficiency by precluding futile efforts. We adopted only three representative stoichiometries, $ARTi_2O_6$ ($Pm\bar{3}m$ or $R\bar{3}c$), $ARTiO_4$ ($P4/nmm$ or $Pbcm$), and $A_2R_2Ti_3O_{10}$ ($I4/mmm$), which consist of simple numbers of x, y, and z. It should be noted that the database was provided with far more stoichiometries of different structures consisting of more-complicated numbers. Nonetheless, our choice of only the three simplest stoichiometries seems plausible, considering the fact that almost all of the well-known commercial phosphors have such a simple stoichiometry. We admit that the GACC screening within a limited well-known composition range might raise some questions, because good intuition as the result of plenty of experience along with the correct knowledge of the physics and chemistry of materials might lead us to a correct decision more easily and promptly than by using GACC. However, the GACC has some advantages. First, the GACC is a more-systematic approach based on global optimization strategy, so there should be no possibility of mistakes. Second, it should be noted that it does not cost a great deal to prepare such a large number of samples because of the well-developed high-throughput experimentation system that we have developed,[15−21] even though it might appear to be a waste of effort, cost, and time.

The random process produced a population of 54 in the first generation. Considering the simulation results,[5] a population size of 54 was sufficient for complete optimization, even though we adopted a larger population size (108) in our previous report.[4] Only three sets of x, y, and z were adopted, and the composition code was separated into existence and composition codes to reduce the composition dimensionality. We also employed an additional parameter that described the excessive amount of alkali metals. As a result, the optimization was implemented in 10-dimensional parameter space, two of which (xyz and existence) are categorical parameters and the rest (composition and excessive amount) are numeric parameters. Figure 1a shows the parameters adopted for use in the present GACC process. Evolutionary operations such as elitism, selection, crossover, and mutation were then applied to this first generation using actually measured luminescence values of all the members in the first generation. This computational evolutionary process yielded another new library, with the same number of new compositions as the first one, which is referred to as the second generation. The second generation showed a somewhat-improved luminescence. The same processing was done

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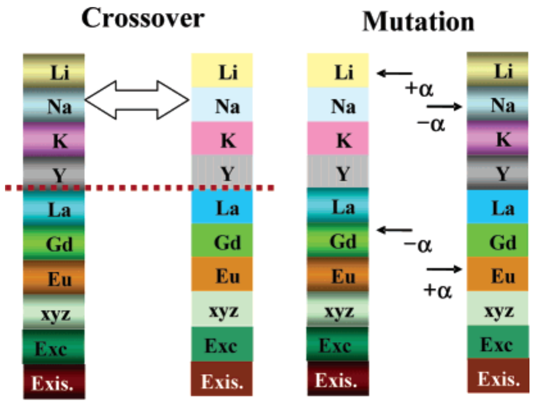

Figure 1. Schematic description of the parameters used for the genetic algorithm and the crossover and mutation operations.

on the second generation and yielded the third generation and so on. This process will improve the luminescence of all members of the generation as the generation number increases, finally leading us to the optimum. Namely, the GACC is implemented by repeating the experiment and the computational evolutionary operation in turn.

The selection, crossover, and mutation rates were all set at 100%, and the roulette-wheel selection was adopted. Elitism was also involved; that is, the highest two compositions in the former generation were elicited and copied to the next generation. Elitism plays a significant role not only in preserving the excellent members but also in checking the experimental consistency in the case of experimental evolutionary processes. Namely, by incorporating the copied members into the next generation, they can serve as an effective indicator for examining the consistency of the synthesis process of each generation. If these copied members show a discrepancy between generations, then the validity of the experiment would not be reliable. The single-point crossover was adopted, and the crossover point was determined randomly. The mutation was achieved by adding and subtracting a random number for two arbitrarily chosen components. The crossover and mutation operations 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 these was shaded in order to permit discrimination between them and hence to trace them out after the crossover. They were treated as chromosomes, and the element sectors were regarded as genes. The crossover created offspring by exchanging the genes of the parents, and subsequent mutational operations were executed on these offspring. We developed the above-described GACC process using the Microsoft visual basic platform.

Results and Discussion

The inset in Figure 2 shows photographs of the first and fifth generations taken under an excitation wavelength of 365 nm. The lamp light was illuminated evenly over the library, so that a relative comparison could be made. It should be noted that the excitation light wavelength of the lamp (365 nm) differs from the 400 nm excitation that was adopted for use in quantitative measurements. In contrast to our previous reports,[4,6] only a slight improvement can be recognized, judging from appearances. In fact, the overall luminescence level of the first generation was considerable, because we adopted three plausible fundamental stoichiometries, which had been expected to show a certain degree of luminescence even in the first generation. It should be noted that the goal of the present GACC process was not to examine whether luminescence can be seen but to pinpoint the best member among the candidates, all of which show a certain level of luminescence. Thus, the GACC is the best way of dealing with this type of sophisticated screening. On the other hand, a large-scale, high-throughput screening on the basis of thin-film libraries would be favorable for the very early stages of screening, in which case the issue of whether luminescence takes places can be dealt with.

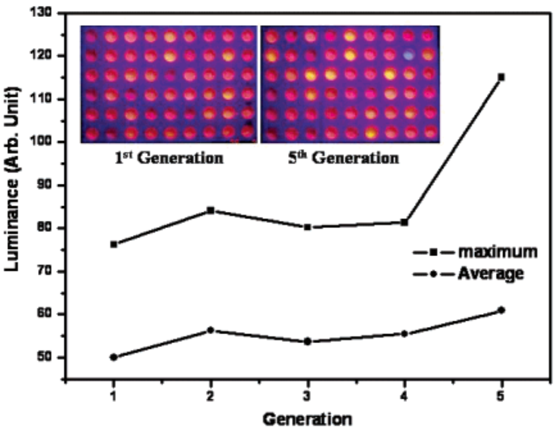

Figure 2. Maximum and average luminescence as a function of generation number at a 400 nm excitation. The inset shows libraries of both the first and fifth generation at a 365 nm excitation.

Figure 2 also shows quantitative results, in which the highest and average luminescence values of each generation are plotted as a function of generation number. As can be seen in Figure 2, both values increase slightly at the early stage of the evolutionary process, decrease at the third generation, and are eventually promoted at the fifth generation. The composition of the maximum luminescence was identical both in the second and third generations by elitism, and the decrease was negligible (within 5%). The fact that the same decreasing ratio was shown in both the maximum and average luminescence led us to conclude that the drop in luminescence can be attributed to experimental error. Because of this, it was ignored, and the data from the third generation was used to produce the next generation. In fact, it is the rank that is more important than the luminescence value itself in the genetic algorithm. Thus, such an overall degradation with the rank unchanged would never have any negative influence on the computational process. We have often been confronted with such a slight drop in other actual GACC implementations and it was due to experimental errors, so it can be ignored, unless the luminescence drop exceeds 5%. We stopped the GACC process at the fifth generation, when a significant enhancement was obtained. According to our past experiences,[4,6] the maximum luminescence would become saturated at later generations. Consequently, the composition of the highest luminescence was approximated to a composition of $(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO_4{:}Eu^{3+}$. The Eu^{3+} doping content was 0.2 mol, substituting for yttrium and gadolinium. The GACC automatically weeded out useless elements (La and K) by the evolutionary principle. The top five compositions (top 10%) in the fifth generation do not deviate greatly from the composition of the highest luminescence. This verifies that

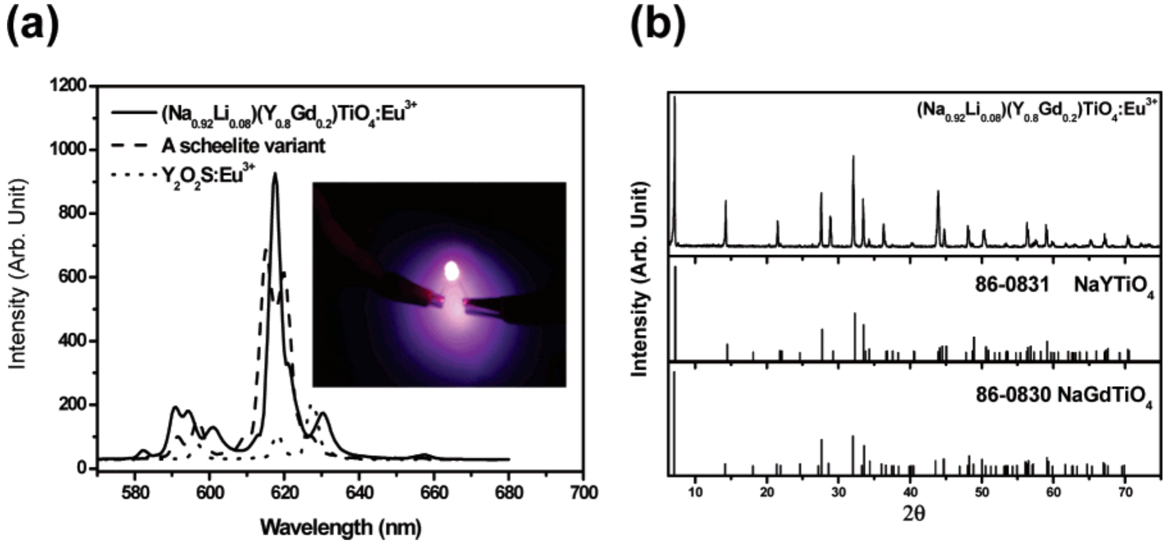

Figure 3. (a) Emission spectra of $(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO_4:Eu^{3+}$ and the scheelite variant phosphor and $Y_2O_2S:Eu^{3+}$ for comparison. (b) X-ray diffraction pattern of $(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO_4:Eu^{3+}$ along with standard data. The inset in (a) shows a photograph of a red LED consisting of an InGaN chip and $(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO_4:Eu^{3+}$ phosphor powder at 20 mA and 3.3 V.

evolutionary optimization clearly took place during our experimental process. Rather than proceeding with the GACC process beyond the fifth generation, we secured the reproducibility of this final composition by the conventional solid-state reaction method, which is more useful for mass production from a practical point of view. At the same time, we examined some other compositions in the vicinity of this final composition by the conventional solid-state reaction method. As a result, these findings reconfirmed that the luminescence of the $NaYTiO_4:Eu^{3+}$ phosphor was better than that of the $NaGdTiO_4:Eu^{3+}$ phosphor and also that it improved when codoped with Li and Gd. Consequently, it was concluded that our final composition obtained from the GACC process was a real optimum in the given parameter space. The detailed results of these auxiliary experiments are presented in the Supporting Information.

Figure 3a shows the emission spectra of $(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO_4:Eu^{3+}$ at the 400 nm excitation, along with commercially available $Y_2O_2S:Eu^{3+}$ (Nichia) and a well-known scheelite variant phosphor, provided by the Samsung Electronics Co. Ltd. The luminescence of $(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO_4:Eu^{3+}$ was greater than that of a scheelite variant phosphor by about 10%. Thus, $(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO_4:Eu^{3+}$ could be applicable for use in tricolor white LEDs on the basis of this result. Several red LEDs were also produced by using $(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO_4:Eu^{3+}$ powders and InGaN chips in an attempt to examine whether the luminescence of the $(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO_4:Eu^{3+}$ phosphor is also promising under the actual LED environment. The inset in Figure 3a exhibits one of these red LEDs electrically driven at 20 mA and 3.3 V, in which strong red emission can be observed, even though the InGaN chip emission was not at 400 nm but at 390 nm. As a result, the applicability of this new phosphor to white LEDs was confirmed. It is also worthwhile to consider the structural analysis of $(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO_4:Eu^{3+}$. The XRD data in Figure 3b show that the $(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO_4:Eu^{3+}$ composition crystallized into the $ARTiO_4$ structure (layered Perovskite in the *Pbcm* symmetry). It should be noted that the structures of these types of compounds have been well-known for decades,[22−26] and even $NaGdTiO_4:Eu^{3+}$ was once considered to be a red phosphor.[23] However, $ARTiO_4$-based phosphors have been out of concern for decades because they do not have an efficient absorption band at around 254 nm.

It should be noted that 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 well-known compounds in order to maximize the property of concern. In fact, there should be very few phases that remain unknown in such a simple ternary or quaternary cation system, because most of the tangible stoichiometric compounds are already well-known. In addition, it is obvious that almost all phosphors that are currently used in recently developed applications such as plasma display panels (PDP) and white LEDs, e.g., BAM: Eu^{2+}, $Zn_2SiO_4:Mn^{2+}$, $(Y,Gd)BO_3:Eu^{3+}$, and $YAG:Ce^{3+}$, were not newly developed in an attempt to apply them specifically for PDPs and LEDs but for some other old-fashioned applications long ago. This means that new requirements for new applications made it possible to discover new functionalities from these materials and to fully adapt them to new applications. In this regard, the GACC is an excellent tool for extracting a new functionality from well-known compound systems and optimizing their use. The GACC approach adopted in the present investigation revealed that the $ARTiO_4$-based system has some promise as red phosphors for tricolor white LEDs and, in turn, permits the sophisticated composition to be fine-tuned to achieve more promising luminescence. It is our opinion that the GACC is a very efficient and practical method for searching for new materials for a specific use. In a certain extreme instance, the GACC might facilitate the search process for new materials in a

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much-faster time frame than that of conventional searches of the literature for appropriate information.

Conclusions

In summary, the GACC process made it possible to facilitate the search process for new oxide-based red phosphors for use in tricolor LEDs. The composition of the maximum luminescence was determined to be $(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO_4:Eu^{3+}$. As a result of phase identification, the main phase of the optimum composition $(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO_4:Eu^{3+}$ was proven to be layered Perovskite in the *Pbcm* symmetry. The luminescence of $(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO_4:Eu^{3+}$ was 110% of that of the scheelite variant phosphor at an excitation of 400 nm. Consequently, it might be possible to adopt this new phosphor as a red phosphor for tricolor white LED applications, if the luminescence were enhanced slightly by optimizing some extrinsic properties such as powder size and shape.

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Supporting Information Available: Tables showing the compositions and corresponding luminescence of the five generations discussed in the paper (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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