

Search for new phosphors for flat panel displays and lightings using combinatorial chemistry and computational optimization

Kee-Sun Sohn*, Yu Sun Jung, Sang Ho Cho, Chandramouli Kulshreshtha
 Department of Materials Science and Metallurgical Engineering, Suncheon National University, Korea

Phone:82-61-750-3557, E-mail: kssohn@sunchon.ac.kr

Abstract

An evolutionary optimization process involving genetic algorithm and combinatorial chemistry was employed in an attempt to develop titanate-based red phosphors suitable for tri-color white light emitting diodes. We screened a eight-cation oxide system including $(K, Li, Na)_x(Y, Gd, La, Eu)_yTi_zO_\delta$ in terms of luminescent efficiency. The combination of genetic algorithm and combinatorial chemistry was proven to enhance the searching efficiency when applied for phosphor screening. As a result, the composition was optimized to be $(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO_4:Eu^{3+}$. The luminance of this phosphor was 110 % of that of well-known scheelite variant phosphor at an excitation of 400 nm.

1. Introduction

White light emitting diodes (LEDs) have been considered as good general lighting devices based on the possibility that their substitution for fluorescent or incandescent lamps would lead to considerable energy saving. The combination of blue chip and yellow phosphor has been already developed and commercially available, but tri-color white LEDs consisting of a soft-UV chip emitting 400 nm wavelength and red, green and blue (RGB) phosphors is still a challenge [1~3]. In the case of the tri-color white LED, the inorganic oxide compound would be the best candidate for the RGB phosphors in terms of both chemical stability and luminescent efficiency. However, no promising red oxide phosphors have been found yet, whereas there are some good candidates for green and blue phosphors. Thus, the development of a good red phosphor is a key technology in achieving the tri-color white LED lighting system. In this regard, there have been several attempts to develop oxide red phosphors [4~8]. We have developed a red phosphor in oxyapatite structure by employing an evolutionary optimization strategy

[4~6]. In addition, Neeraj et al. also found more promising oxide red phosphors for tri-color white LEDs, which are in scheelite and westfieldite structures [7,8]. The scheelite red phosphor was proved to be the best among those developed so far. However, we need more efficient red phosphors to achieve an acceptable efficiency of white LED. In this regard, we need a new, smart strategy to develop new red phosphors. The genetic algorithm – assisted combinatorial chemistry (GACC), combining a computational evolutionary optimization strategy and high-throughput synthesis and characterization processes, was employed to develop new red phosphors for tri-color white LEDs. Our final goal was to develop a new red phosphor, the luminescent efficiency of which should exceed that of the scheelite phosphor. For this sake, we screened and optimized 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 due to its ability to compensate for the weak points in the traditional high through-put combi-chem in the pharmaceutical research area [9~11]. When the area of inorganic material synthesis and screening is concerned in association with GACC, it 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 a search for heterogeneous catalysts based on inorganic oxide system. More importantly, it is noted that inorganic phosphors are more suitable for the GACC method by invoking the fact that the screening process can be greatly facilitated compared to that for catalysts. In this regard, we have employed this strategy to develop inorganic phosphor materials for the first time [4,6]. According to our previous report dealing with red phosphors for tri-color white LEDs [4,5], even though we started with thoroughly random

108 compositions, the evolutionary process ended up with a well-crystallized single phase (Oxyapatite) in the sixth generation [5]. But it was unfortunate that even though we confirmed the effectiveness of the GACC for the development of phosphors, the final product had no practical use. In the present investigation, however, we aimed to develop promising new red phosphors, the luminescent property of which is acceptable from the practical point of view, so that they can be applied to actual applications promptly.

2. Results

The evolutionary optimization was implemented in the multi-composition (multi-parameter space) system, i.e. $(K, Li, Na)_x(Y, Gd, La, Eu)_yTi_zO_8$. There could be a large number of stoichiometric compounds (single-phase line compounds) along with a huge number of their solid solutions and their mixtures in this eight-dimensional composition system. Unlike our previous case where completely random compositions were adopted [4,6], the fundamental stoichiometry x , y , and z were set as several combinations of simple prime numbers, which was elicited from well-known data bases such as inorganic crystal structure database (ICSD) and joint committee for powder diffraction standards (JCPDS). As a result, the evolutionary optimization process was confined this significantly reduced parameter space, which enhanced the searching efficiency by precluding futile efforts and also guaranteed every single member in any generation a certain crystalline structure.

The GACC begins with 54 random compositions in the $A_xR_yTi_zO_8$ ($A = K, Li, Na, R = Y, Gd, La, Eu$) system. As already mentioned, the numbers x , y , and z were chosen among well-known stoichiometries taken from ICSD and JCPDS data base. We only adopted three representative stoichiometries such as $ARTi_2O_6$ ($Pm\bar{3}m$ or $R\bar{3}c$), $ARTiO_4$ ($P4/nmm$ or $Pbcm$) and $A_2R_2Ti_3O_{10}$ ($I4/mmm$), which consists of simple prime numbers of x , y , and z . It should be noted that the data base provided with far more stoichiometries of different structures consisting of more complicated numbers. Nonetheless, our choice of only the three simplest stoichiometries seems plausible by considering the fact that almost all of well-known commercial phosphors have such a simple stoichiometry. We admit that there might be a skepticism about the GACC screening within a limited well-known composition range, because good

intuition originating from a plenty of experience along with correct knowledge about physics and chemistry of materials might lead us to a right decision more easily and promptly than the case of GACC. However, it is worth while to employ the GACC for the following reasons. Firstly, the GACC is more systematic approach based on global optimization, so that there is no possibility of mistake. Secondly, it should be noted that it does not cost a great deal to prepare such a huge number of samples owing to the well-developed experimentation system that we secured [15~21], even though it looks like a kind of waste of efforts, cost and time.

The random process produced the first generation, the population of which is 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 the practical point of view, i.e., the population size of 54 is good enough for complete optimization, even though we have adopted larger population size (108) in our previous report [4]. Only three choice of x , y and z values was adopted and the composition code was separated into existence and composition codes to reduce the composition dimensionality. We also employed an additional parameter describing the excessive amount of alkali metals. As a result, the optimization was implemented in the ten-dimensional parameter space, two of them (xyz and existence) are categorical parameters and the rest of them (composition and excessive amount) are numeric parameters. Fig. 1 (a) shows the parameters adopted in the present GACC process. 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 of the same number of new compositions as the first one, which is called the second generation. 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 based on the measurement results. It should

be, however, noted that we often confront a slight drop in luminance even in the later generation in the actual GACC implementation. This was due to experimental errors, so that we can ignore it unless the luminance drop exceeds 5 %. We also observed such a slight decrease both in maximum and average luminance between the second and third generations in the present investigation as can be seen in Fig. 2. However, the luminance drop was within 5 %, so that we could proceed without any reconsideration.

The selection, crossover and mutation rates were all set at 100 %. The roulette wheel selection was adopted. The elitism was also involved, that is, the highest two compositions in the former generation were elicited and copied to the next generation. The 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. If these copied members showed a discrepancy between generations, then the validity of the experiment would never 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 arbitrary chosen components, respectively. The operation of crossover and mutation were described schematically in Fig. 1 (a). Two parent members chosen by the roulette wheel selection method were represented as composition bands as can be seen in Fig. 1 (a). One of them was shaded in order to make 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 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 were executed on these offspring. Fig. 1 (b) shows the computational tool that we developed for the GACC using MS visual basic platform.

The inset into Fig. 2 shows the photographs of the first and fifth 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. It is noted that the excitation light wavelength of the lamp (365 nm) differs from the 400 nm excitation that was adopted for quantitative measurements. In

contrast to our previous reports [4,6], we can hardly recognize a remarkable improvement by judging by appearances. In fact, the overall luminance level of the first generation was even considerable, since we only adopted three plausible stoichiometries, which had been expected to show a certain degree of luminance, in the first generation. It should be noted that what really matters in the present investigation was not to examine whether we can see the luminescence or not but to pinpoint the best member among those, all of which show a certain level of luminescence. Thus the GACC is the best way of dealing with this kind of sophisticated screening. On the other hand, a large scale screening based on thin film libraries is favorable for very early stage of screening, in which case a matter of whether or not the luminescence is activated can be dealt with.

Fig. 2 also 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 Fig. 2, both values slightly increase at the early stage of the evolutionary process and decrease at the third generation and eventually promote at the fifth generation. The composition of maximum luminance was identical both in the second and third generations by the elitism and the decrease was negligible (within 5 %). The fact that the same decreasing ratio was shown in both the maximum and average luminance led us to a conclusion that the luminance drop was ascribed to experimental error, so that we ignored it and used the data from the third generation for the computational evolutionary process to produce next generation. As a matter of fact, it is the rank that is more important than the luminance value itself in the genetic algorithm, so that such an overall degradation with the rank unchanged would never have any negative influences on the computational process. We stopped the GACC process when a significant enhancement was obtained at the fifth generation. According to our past experiences [4,6], we expected that the maximum luminance would saturate at later generations. Consequently, the composition of the highest luminance was approximated to a composition $(\text{Na}_{0.92}\text{Li}_{0.08})(\text{Y}_{0.8}\text{Gd}_{0.2})\text{TiO}_4:\text{Eu}^{3+}$ and regarded it as a final composition. The Eu^{3+} doping content is 0.3 mol substituting for yttrium and gadolinium. Instead of proceeding on the GACC, we secured a reproducibility of this final composition by the conventional solid state reaction method, which is

practically more essential for the mass production. At the same time, we also implemented auxiliary experiments to examine some other compositions at the vicinity of this final composition by the conventional solid state reaction method. As a result, it was reconfirmed that our final composition obtained from the GACC process was an optimum in the given parameter space. The detailed results from these confirmative experiments were not presented here for the compactness of the manuscript. The GACC weeds 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 eight-cation system, La and K was rapidly weeded out and thus the composition of the highest luminance was fixed at $(\text{Na}_{0.92}\text{Li}_{0.08})(\text{Y}_{0.8}\text{Gd}_{0.2})\text{TiO}_4:\text{Eu}^{3+}$. The top five compositions (top 10 %) in the fifth generation do not deviate greatly from the composition of the highest luminance. This proved that the evolutionary optimization certainly took place during our experimental process.

From the practical point of view, it is more important to investigate how promising the luminance level of the best member $(\text{Na}_{0.92}\text{Li}_{0.08})(\text{Y}_{0.8}\text{Gd}_{0.2})\text{TiO}_4:\text{Eu}^{3+}$ and to identify the exact structure. Fig. 3 (a) shows the emission spectra of $(\text{Na}_{0.92}\text{Li}_{0.08})(\text{Y}_{0.8}\text{Gd}_{0.2})\text{TiO}_4:\text{Eu}^{3+}$, along with a well-known Scheelite variant phosphor for comparison. The luminance of $(\text{Na}_{0.92}\text{Li}_{0.08})(\text{Y}_{0.8}\text{Gd}_{0.2})\text{TiO}_4:\text{Eu}^{3+}$ was slightly higher by about 6 % than a Scheelite variant phosphor, which was provided by Samsung electronics Co. Ltd. Even though $(\text{Na}_{0.92}\text{Li}_{0.08})(\text{Y}_{0.8}\text{Gd}_{0.2})\text{TiO}_4:\text{Eu}^{3+}$ is not greatly superior to the Scheelite variant phosphor, $(\text{Na}_{0.92}\text{Li}_{0.08})(\text{Y}_{0.8}\text{Gd}_{0.2})\text{TiO}_4:\text{Eu}^{3+}$ could be applicable to tri-color white LEDs. It is also worth while to consider the structural analysis of $(\text{Na}_{0.92}\text{Li}_{0.08})(\text{Y}_{0.8}\text{Gd}_{0.2})\text{TiO}_4:\text{Eu}^{3+}$. According to XRD data in Fig. 3 (b), the $(\text{Na}_{0.92}\text{Li}_{0.08})(\text{Y}_{0.8}\text{Gd}_{0.2})\text{TiO}_4:\text{Eu}^{3+}$ composition included a main phase in the *Pbcm* symmetry and also minor phases, the amount of which was negligible though. As we had expected, the structure of the main phase is based on ARTiO_4 (layered Perovskite in the *Pbcm* symmetry). It should be noted that the structure of this type of compounds has been well known for decades [] and even $\text{NaGdTiO}_4:\text{Eu}^{3+}$ has been once considered as a red phosphor []. But the ARTiO_4 -based phosphors have

been out of concern for decades because they do not have efficient absorption band at around 254 nm.

It should be noted that the substantial goal of the GACC, in view of practicality, is not to find a completely new compound but to endow well-known compounds a new functionality in relation to newly developed applications, and also 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 tangible stoichiometric compounds have been already well known. In addition, it is obvious that almost all phosphors currently used for recently developed applications such as plasma display panels (PDP) and white LEDs, e.g., $\text{BAM}:\text{Eu}^{2+}$, $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$, $(\text{Y,Gd})\text{BO}_3:\text{Eu}^{3+}$ and $\text{YAG}:\text{Ce}^{3+}$, were not newly developed in an attempt to apply them only for PDPs and LEDs but they had been developed for some other old fashioned applications. 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 helped us extract a new functionality from the ARTiO_4 -based phosphors, which implies that they were found to be promising red phosphors for tri-color white LED. Furthermore, the GACC fine-tuned the composition very efficiently to achieve more promising luminance, so that it was revealed that the luminance of $\text{NaYTiO}_4:\text{Eu}^{3+}$ phosphor was better than that of $\text{NaGdTiO}_4:\text{Eu}^{3+}$ phosphor and also it was improved when co-doped with Li and Gd. This new finding was also reconfirmed by the auxiliary, confirmative experiments based on the solid state reaction method. Accordingly, the usability of GACC strategy was validated to be very promising in comparison to conventional approaches. Our concrete opinion is that the GACC is a much more efficient and practical way of searching for new materials for a specific use. For a certain extreme instance, the GACC might facilitate the searching process for new materials in a much faster manner rather than ransacking hackneyed literatures for appropriate information.

3. Conclusion

In summary, the GACC process made it possible to facilitate the search process for a new oxide based red phosphor for use in tri-color LEDs. The composition of the maximum luminance was determined to be

(Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO₄:Eu³⁺ in a five-generation process. 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})TiO₄:Eu³⁺ was proven to be layered Perovskite in the *Pbcm* symmetry. The luminance of (Na_{0.92}Li_{0.08})(Y_{0.8}Gd_{0.2})TiO₄:Eu³⁺ was 106 % of that of Scheelite variant phosphor at 400 nm excitation. Consequently, it could be possible to adopt this new phosphor as a red phosphor for tri-color white LED applications, if the luminance were enhanced slightly by optimizing some extrinsic properties such as powder size and shape.

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5. References

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Table 1. Details about the Solutions Used in the Precursor Delivery

Solution	Li ₂ CO ₃ (Aldrich) + 2% HNO ₃	Na ₂ CO ₃ (Kojundo) + deionized water	K ₂ CO ₃ (Kojundo) + deionized water	Y ₂ O ₃ (Kojundo) + 8% HNO ₃	Gd ₂ O ₃ (Kojundo) + 10% HNO ₃	Ti(OC ₂ H ₅) ₄ (Aldrich) + Ethanol	Eu ₂ O ₃ (Kojundo) + 11% HNO ₃
Metal Concentration	0.5 M	0.5 M	0.5 M	0.5 M	0.5 M	0.5 M	0.5 M

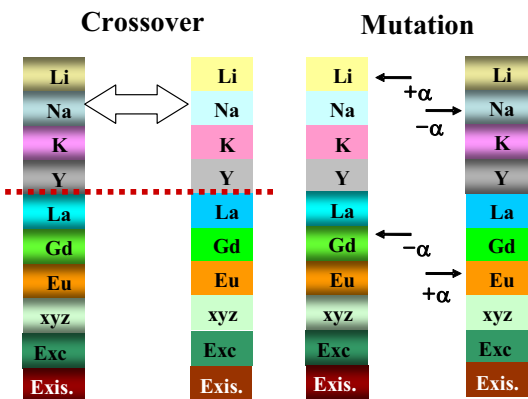


Fig. 1. Schematic description of the parameters used for the genetic algorithm and the crossover and mutation operations

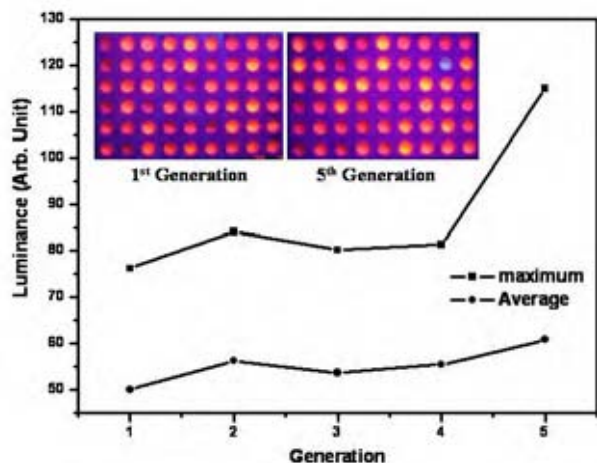


Fig. 2. Maximum and average luminance as a function of generation number at a 400 nm excitation. The inset shows libraries of both the first and fifth generation at a 365 nm excitation.

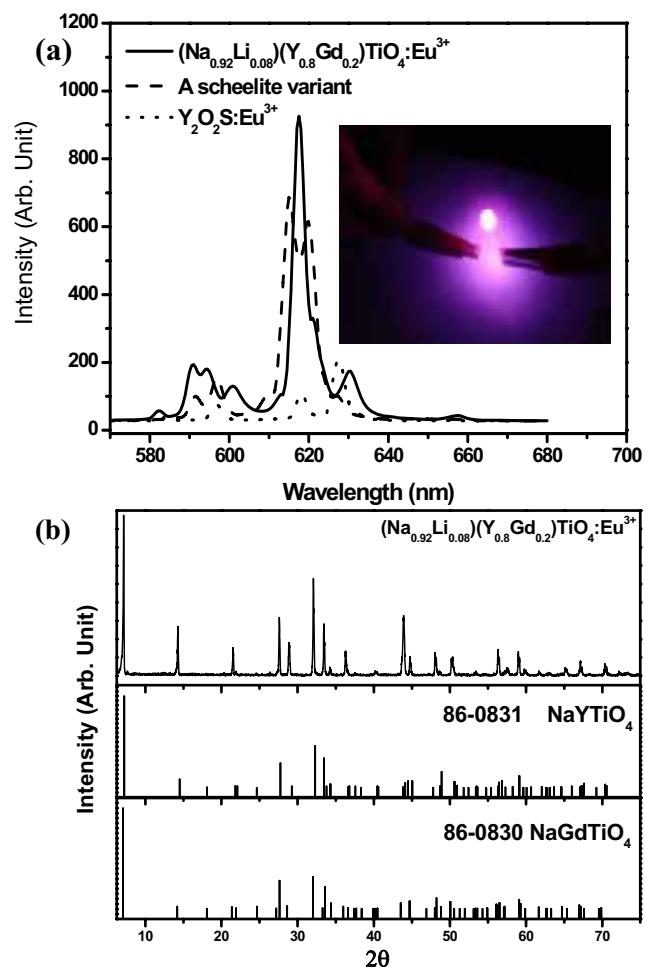


Fig. 3. (a) Emission spectra of $(\text{Na}_{0.92}\text{Li}_{0.08})(\text{Y}_{0.8}\text{Gd}_{0.2})\text{TiO}_4:\text{Eu}^{3+}$ and the scheelite variant phosphor and $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ for comparison, and (b) X-ray diffraction pattern of $(\text{Na}_{0.92}\text{Li}_{0.08})(\text{Y}_{0.8}\text{Gd}_{0.2})\text{TiO}_4:\text{Eu}^{3+}$ along with standard data. The inset in (a) shows a photograph of red LED consisting of InGaN chip and $(\text{Na}_{0.92}\text{Li}_{0.08})(\text{Y}_{0.8}\text{Gd}_{0.2})\text{TiO}_4:\text{Eu}^{3+}$ phosphor powder at 20 mA and 3.3 V.