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RESEARCH ARTICLE

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Solid-State Combinatorial Screening of $(Sr,Ca,Ba,Mg)_2Si_5N_8:Eu^{2+}$ Phosphors

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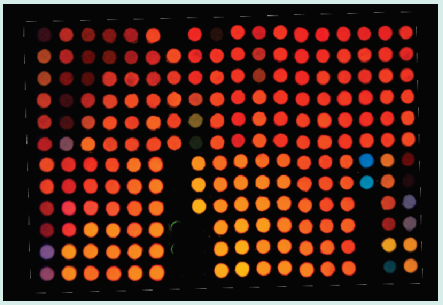
Supporting Information

ABSTRACT: We employed a solid-state combinatorial chemistry technique to screen 4 ternary phosphor systems: $(Sr,Ca,Ba)_2Si_5N_8:Eu^{2+}$, $(Sr,Ca,Mg)_2Si_5N_8:Eu^{2+}$, $(Sr,Mg,Ba)_2Si_5N_8:Eu^{2+}$, and $(Ca,Ba,Mg)_2Si_5N_8:Eu^{2+}$. The current pure nitride-based system did not allow for the use of conventional liquid solution-based high-throughput experimentation, so that a specially designed solid-state high-throughput powder-dispensing synthesis technique was employed. As a result, four well-defined ternary combinatorial libraries were developed in terms of photoluminescent (PL) intensity and color chromaticity with no skipped compositions, which provided a quantitative relationship between PL properties and the composition of $AE_2Si_5N_8:Eu^{2+}$ (AE = alkaline earth elements) phosphors.



KEYWORDS: combinatorial chemistry, phosphor, LED

INTRODUCTION

Nitride phosphors have recently attracted considerable attention for their use in phosphor-converted white light emitting diodes (ps-WLED). When a red or amber color of light-emitting phosphors are used in pc-WLED, nitrides such as $MAlSiN_3:Eu^{2+}$ or $M_2Si_5N_8:Eu^{2+}$ (M = alkaline earth elements) phosphors[1−5] have been successfully commercialized and have exhibited better performance than oxide phosphors in terms of luminescent efficacy, color rendering, thermal stability, etc. In particular, the present investigation focused on $M_2Si_5N_8:Eu^{2+}$ phosphors, which hereafter will be referred to as 2−5−8. Although the structural and luminescent properties of several 2−5−8 phosphors have been investigated in a limited composition range,[2−5] the full composition range consisting of representative alkaline earth elements such as Mg, Ca, Sr, and Ba deserves to be examined in more detail. The literature[4,5e,5f] notes the fragmentary composition range that the aforementioned alkaline earth elements constitute. However, detailed PL and structural data in such a full composition range have never been reported. Therefore, we researched four ternary phosphor composition ranges, $(Sr,Ca,Ba)_2Si_5N_8:Eu^{2+}$, $(Sr,Ca,Mg)_2Si_5N_8:Eu^{2+}$, $(Sr,Mg,Ba)_2Si_5N_8:Eu^{2+}$, and $(Ca,Ba,Mg)_2Si_5N_8:Eu^{2+}$, established well-defined ternary libraries in terms of structure, PL intensity and color chromaticity, and obtained a quantitative composition property relationship (QCPR) in the full range of all these ternary compositions. The terminology, both binary and ternary, represents only alkaline earth compositions in the present investigation.

It would be difficult to synthesize a large number (203) of ternary phosphors using the conventional one-by-one synthesis strategy in a limited time period. Therefore, a combinatorial chemistry (combi-chem) approach based on high-throughput processes would be most helpful in achieving the complete screening of the ternary phosphors of concern in a short period of time. In fact, we completed the synthesis and characterization of 203 phosphors in only one week using a combi-chem technique. The combi-chem approach to pure nitride phosphors requires special care. The conventional liquid solution-based combi-chem technique, which is known to be versatile for various material systems, such as oxide-based phosphors[6] and heterogeneous catalysts,[7] cannot be applied to the nitride system because some of the starting materials are extremely susceptible to an ambient atmosphere that includes moisture, and, therefore, they should never be dissolved in aqueous solvents. Therefore, we built up a solid-state combi-chem process involving a solid-state high-throughput dispensing system in an inert atmosphere with the subsequent high-throughput mixing, grinding, and, eventually, firing processes that could be implemented in a dry environment. Considering the fact that almost all commercially available powder phosphors are prepared using solid-state reaction methods, the present solid-state combinatorial approach was more pragmatic than the conventional liquid solution-based combinatorial approach in terms of scale-up and commercialization. This means that we could guarantee reproducibility, even if the conventional solid-state reaction method was adopted with an increased synthesis

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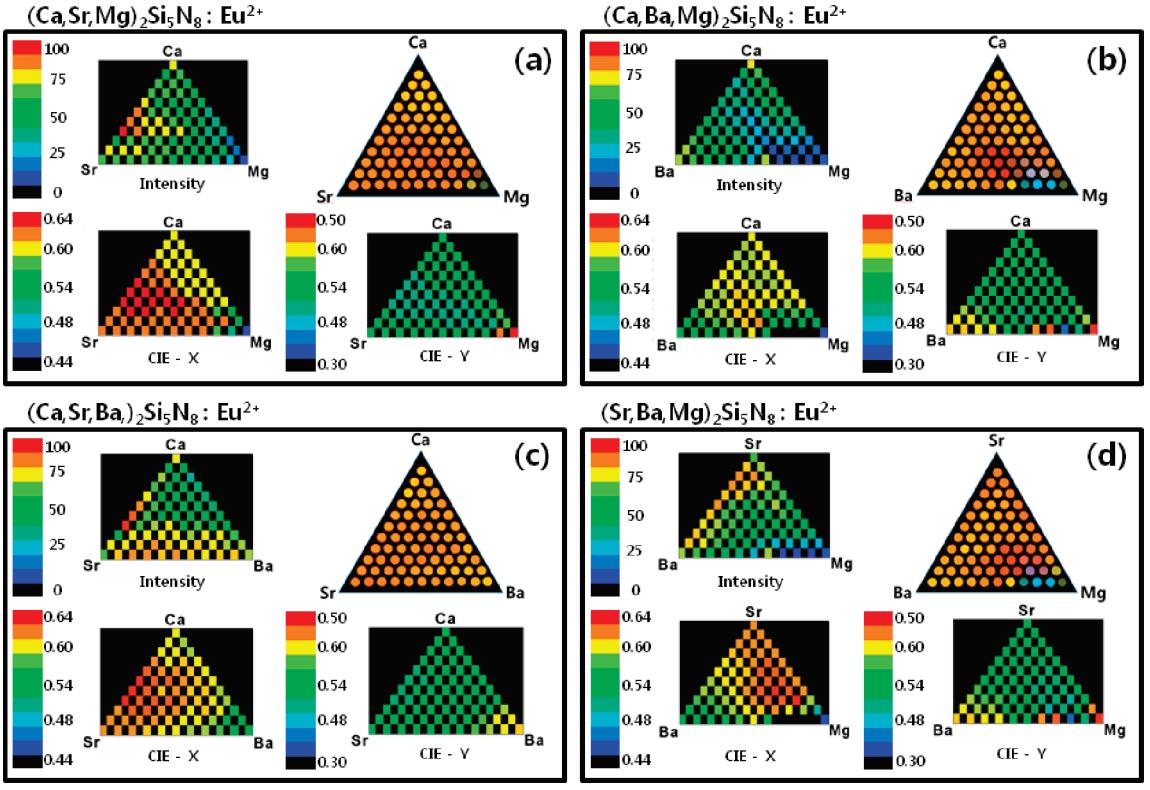

Figure 1. Ternary combi-chem libraries for (a) $(Ca,Sr,Mg)_2Si_5N_8:Eu^{2+}$, (b) $(Ca,Ba,Mg)_2Si_5N_8:Eu^{2+}$, (c) $(Ca,Sr,Ba)_2Si_5N_8:Eu^{2+}$, and (d) $(Sr,Ba,Mg)_2Si_5N_8:Eu^{2+}$ in terms of photoluminescent intensity and color chromaticity. Actual photos taken under 365 nm excitations are also presented.

volume for every sample in the ternary library. In fact, the discrepancy between the small-scale combi-chem library sample and the conventionally synthesized, large-scale sample is considered to be the most serious drawback of combinatorial chemistry as far as inorganic compounds are concerned.[6d] It is our opinion that such inconsistency has been problematic in both liquid solution (inkjet printing)-based combi-chem and thin-film technology-based combi-chem.

EXPERIMENTAL PROCEDURES

The commercially available starting nitrides in the powdered state, Mg_3N_2 (Aldrich, 99.5%), Sr_3N_2 (Kojundo, 99%), Ca_3N_2 (Aldrich, 95%), Ba_3N_2 (Cerac, 99.7%), α-Si_3N_4 (Aldrich, purity unreported), and EuN (Kojundo, 99.9%) were separately ground manually for several hours before the mixing process. The raw powders were dispensed according to predetermined compositions, and were then dry mixed in a high-throughput way using a robotic platform (Swave, ChemSpeed Tech Co., Ltd.) in a glovebox with oxygen and a moisture content that was maintained below 2 ppm. A so-called combi-chem container, a specially designed sample container made of BN, which involved 18 sample sites with 8.5 mm in diameter and 18 mm in depth, was devised for the high-throughput dispensing, mixing, grinding, and firing of a large number of samples. The total amount of raw materials at each sample site was around 0.3 g, which led to a sufficient amount of final phosphor powder available for use in any conventional characterizations. The exact amount of raw materials was weighed and dispensed automatically to the sample site by a powder extruder system. The mixing and grinding was executed by vibrating the combi-chem containers with pins inserted inside the sample sites. The mixed raw materials in the combi-chem container were fired at 1600 °C for 2 h under a pressurized N_2 gas environment (5 atm) in the gas-pressurized sintering (GPS) furnace. Two combi-chem containers, that is, 36 samples, were fired simultaneously. The Eu^{2+} content was fixed at 0.02 mol. The fired samples were ground manually and subjected to X-ray diffraction (XRD). Photoluminescence (PL) was measured to obtain PL intensity (defined as the area under an emission band) and CIE color chromaticity. A video, which shows the entire high-throughput process, is available as Supporting Information.

RESULTS AND DISCUSSION

Graphical representations of the combi-chem results, so-called ternary combi-chem libraries, are shown in Figure 1a−d, along with ternary combi-chem libraries for $(Ca,Sr,Mg)_2Si_5N_8:Eu^{2+}$, $(Ca,Ba,Mg)_2Si_5N_8:Eu^{2+}$, $(Ca,Sr,Ba)_2Si_5N_8:Eu^{2+}$, and $(Sr,Ba,Mg)_2Si_5N_8:Eu^{2+}$. The ternary combi-chem library is presented in terms of PL intensity, CIE color chromaticity x and y values, and the actual photograph of the libraries taken at 365 nm excitations is shown. Although there have been several previous reports mentioning binary phosphors,[3,4,5e,5f] actual data for ternary phosphors have thus far not been reported. The ternary libraries shown in Figure 1a−d provide actual data collected from the high-throughput synthesis and characterization of samples in the complete ternary composition range. These ternary libraries deserve notice since the PL intensity and color chromaticity were given as a function of the accurate composition of host materials, and therefore, a systematic trend in QCPR is more easily understood.

Figure 2a−d shows the XRD patterns of four constituent phosphors with their corresponding standard data from the joint

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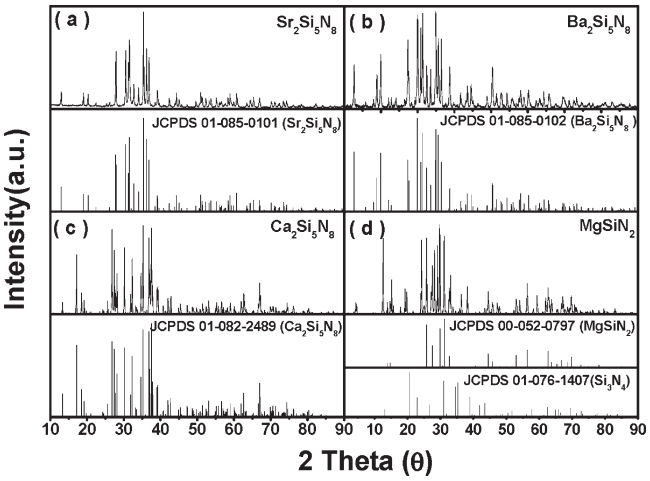

Figure 2. XRD patterns of four constituent phosphors, (a) Sr-2−5−8, (b) Ba-2−5−8, (c) Ca-2−5−8, and (d) Mg-2−5−8, along with their corresponding standard data from the joint committee on powder diffraction standards (JCPDS).

committee on powder diffraction standards (JCPDS). With the exception of $Mg_2Si_5N_8$:Eu^{2+}, all the other constituent phosphors, such as $Ca_2Si_5N_8$:Eu^{2+}, $Sr_2Si_5N_8$:Eu^{2+}, and $Ba_2Si_5N_8$:Eu^{2+}, exhibited their own structures. $Sr_2Si_5N_8$:Eu^{2+} and $Ba_2Si_5N_8$:Eu^{2+} were isostructures, which have an orthorhombic lattice with the space group $Pmn2_1$. $Ca_2Si_5N_8$:Eu^{2+} was monoclinic structure with the space group *Cc*. However, the Mg-2−5−8 ($Mg_2Si_5N_8$:Eu^{2+}) structure was nonexistent, but the Mg-2−5−8 composition constituted a mixture of $MgSiN_2$:Eu^{2+} and Si_3N_4 impurity. $MgSiN_2$:Eu^{2+} did not emit promising luminescence, but we detected a certain degree of blue light emission originating from (Mg,Ba)SiN_2:Eu^{2+} binary solid solutions, as shown in Figure 1c and d. As far as 2−5−8 phosphors were concerned, $(Sr,Ca)_2Si_5N_8$:Eu^{2+} binary phosphors and $(Sr,Ca,Mg)_2Si_5N_8$:Eu^{2+} ternary phosphors, with a limited amount of Mg, were promising in terms of PL intensity. We finally identified three promising compositions, $(Sr_{0.7}Ca_{0.3})_2Si_5N_8$:$Eu^{2+}$, $(Sr_{0.6}Ca_{0.4})_2Si_5N_8$:$Eu^{2+}$, and $(Sr_{0.6}Ca_{0.3}Mg_{0.1})_2Si_5N_8$:$Eu^{2+}$, which exhibited the three highest PL intensities among 203 samples constituting four ternary combi-chem libraries. The PL intensity of these binary and ternary phosphors was higher than that of the well-known $Sr_2Si_5N_8$:Eu^{2+} phosphor. This means that the $(Sr_{0.7}Ca_{0.3})_2Si_5N_8$:$Eu^{2+}$, $(Sr_{0.6}Ca_{0.4})_2Si_5N_8$:$Eu^{2+}$, and $(Sr_{0.6}Ca_{0.3}Mg_{0.1})_2Si_5N_8$:$Eu^{2+}$ phosphors constituted well-defined solid solutions with local structures around the Eu^{2+} activator that were more favorable for enhanced luminescence. The XRD patterns of the $(Sr_{0.7}Ca_{0.3})_2Si_5N_8$:$Eu^{2+}$, $(Sr_{0.6}Ca_{0.4})_2Si_5N_8$:$Eu^{2+}$, and $(Sr_{0.6}Ca_{0.3}Mg_{0.1})_2Si_5N_8$:$Eu^{2+}$ solid solutions were more like that of $Sr_2Si_5N_8$:Eu^{2+}, as shown in Figure 3. Only the ternary $(Sr_{0.6}Ca_{0.3}Mg_{0.1})_2Si_5N_8$:$Eu^{2+}$ phosphor contained a slight amount of an Si_3N_4 impurity phase.

The three representative solid solutions, $(Sr_{0.7}Ca_{0.3})_2Si_5N_8$:$Eu^{2+}$, $(Sr_{0.6}Ca_{0.4})_2Si_5N_8$:$Eu^{2+}$, and $(Sr_{0.6}Ca_{0.3}Mg_{0.1})_2Si_5N_8$:$Eu^{2+}$, were recognized only for their higher PL intensity by comparison with the three constituent 2−5−8 phosphors and other 2−5−8 solid solutions. It should, however, be noted that this result happened only under the present synthesis and measurement conditions. Our results differed from those of other previous results,[3,4,5e,5f] where the PL intensity of the binary 2−5−8 solid solutions never exceeded that of the well-known constituent

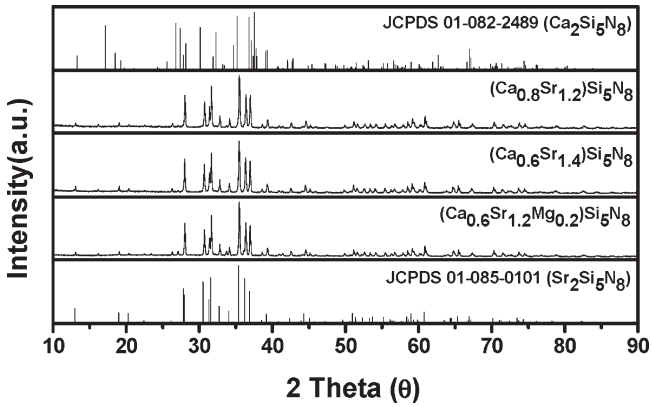

Figure 3. XRD patterns of $(Sr_{0.7}Ca_{0.3})_2Si_5N_8$:$Eu^{2+}$, $(Sr_{0.6}Ca_{0.4})_2Si_5N_8$:$Eu^{2+}$, and $(Sr_{0.6}Ca_{0.3}Mg_{0.1})_2Si_5N_8$:$Eu^{2+}$, along with the standard data for $Sr_2Si_5N_8$:Eu^{2+} and $Ca_2Si_5N_8$:Eu^{2+}.

phosphor $Sr_2Si_5N_8$:Eu^{2+} and $(Sr,Ba)_2Si_5N_8$:Eu^{2+} binary phosphors were better than $(Sr,Ca)_2Si_5N_8$:Eu^{2+} binary phosphors in terms of PL intensity. First of all, our excitation wavelength was 400 nm, whereas the other previously reported data[3,4,5e,5f] were based on 460 or 450 nm excitations. Figure 1 shows that several binary 2−5−8 solid solutions exceeded the well-known constituent phosphor $Sr_2Si_5N_8$:Eu^{2+} in terms of PL intensity at 400 nm excitations. However, the other previous results at 460 or 450 nm excitations differed from the 400 nm excitation data presented here. We could not adopt the conventional 450−460 nm excitations because our combi-chm libraries contained a number of blue-emitting samples. It should be also noted that we adopted 400 nm excitations because the excitation efficiency at 400 nm was higher than those at 450−460 nm according to the excitation spectra in Figure 4. The synthesis condition for our results differed from those of other previous results.[3,4,5e,5f] In addition to the different excitation conditions, the different synthesis routes could be the reason for the discrepancy. In fact, there has been no attempt to synthesize the alkaline earth solid-solution-based 2−5−8 phosphors using the same method that we adopted in the present investigation, even though the well-known constituent phosphor $Sr_2Si_5N_8$:Eu^{2+} has been synthesized using the same method.[2] The present method (GPS in association with pure nitride precursors) is a relatively costly route for synthesizing 2−5−8 phosphors because of the high temperature, the high gas pressure, and the choice of expensive pure nitride precursors. However, the present method is the best in terms of the quality of the final samples, and this method produces the least carbon contamination. Accordingly, a higher PL intensity is both reliable and reasonable for binary and ternary solid solutions when compared with $Sr_2Si_5N_8$:Eu^{2+}.

Figure 4a and b shows the excitation and emission spectra of the three representative binary and ternary phosphors along with those of the constituent phosphors, with the exception of Mg-2−5−8. The emission peaks of the binary and ternary phosphors almost coincided but were red-shifted in comparison with $Sr_2Si_5N_8$:Eu^{2+}. Namely, the peaks were located at a longer wavelength region than were the peaks for any of the constituent phosphors. The binary and ternary phosphors maintained $Sr_2Si_5N_8$ structure, but a considerable amount of Ca was incorporated into Sr site to constitute solid solutions. Because the ionic size of Ca is smaller than Sr, the lattice should be

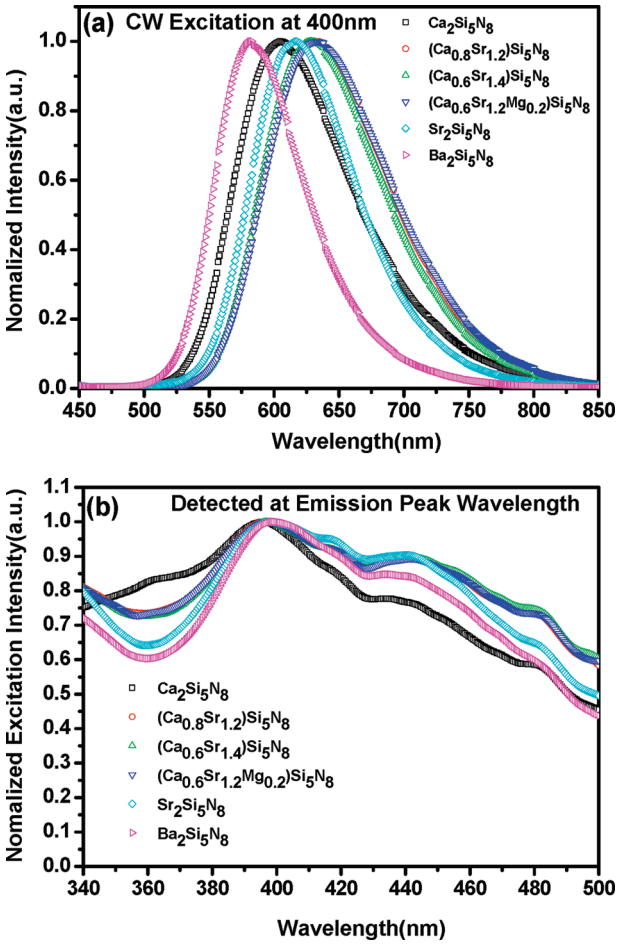

Figure 4. (a) Excitation and (b) emission spectra of $(Sr_{0.7}Ca_{0.3})_2Si_5N_8$:$Eu^{2+}$, $(Sr_{0.6}Ca_{0.4})_2Si_5N_8$:$Eu^{2+}$, and $(Sr_{0.6}Ca_{0.3}Mg_{0.1})_2Si_5N_8$:$Eu^{2+}$ along with those of the constituent phosphors with the exception of Mg-2−5−8.

deflated when Ca is incorporated into the $Sr_2Si_5N_8$ structure. The lattice deflation was confirmed by the XRD data in Figure 3, wherein major XRD peaks of the binary and ternary phosphors slightly shifted toward the high angle side in comparison to the standard data of $Sr_2Si_5N_8$. Consequently, the lattice deflation reduced Eu−N distance and thereby raised crystal field strength and centroid shift (covalency effect) and eventually led to the red shift of the emission band.

In color chromaticity, a red shift equates to a higher CIE *x* value, and the emissions for the binary and ternary phosphors were slightly more red than $Sr_2Si_5N_8$:Eu^{2+}. This would benefit color rendering when applied to pc-WLEDs. Because 2−5−8 phosphors normally emit amber color light, a red shift would be required to secure better color rendering. It is more economical to use Ca and Mg to achieve a red shift than to increase the Eu^{2+} activator content, which is the common way to move the emission band toward the long wavelength side.[1,2] As mentioned above, our Eu^{2+} activator content was fixed at 0.02 mol, which was low enough to save relatively expensive Eu^{2+} source materials. Nonetheless, we maintained a satisfactory red shift without losing luminescent intensity by achieving the binary and ternary solid solutions. In addition, the three representative binary and ternary phosphors showed slightly improved excitation intensity in wavelength ranges longer than 400 nm, to which the conventional LED wavelength belongs. In this regard, the excitation and emission spectral distributions of these representative 2−5−8 phosphors were more suitable for LED applications than other 2−5−8 phosphors appearing in the ternary library.

CONCLUSION

In summary, a solid-state combinatorial chemistry technique was adopted to screen four ternary phosphor systems: (Ca,Sr,Mg)$_2Si_5N_8$:Eu^{2+}, (Ca,Ba,Mg)$_2Si_5N_8$:Eu^{2+}, (Ca,Sr,Ba)$_2Si_5N_8$:Eu^{2+}, and (Sr,Ba,Mg)$_2Si_5N_8$:Eu^{2+}. Although there have been many suggestions and much speculations regarding these ternary phosphors, no actual PL data in the entire composition range of concern have thus far been presented. In the present study, however, we developed the entire ternary composition range, and comprehensively described the quantitative relationship between composition and PL for the 2−5−8 phosphor system. On the basis of this information, three phosphors, $(Sr_{0.7}Ca_{0.3})_2Si_5N_8$:$Eu^{2+}$, $(Sr_{0.6}Ca_{0.4})_2Si_5N_8$:$Eu^{2+}$, and $(Sr_{0.6}Ca_{0.3}Mg_{0.1})_2Si_5N_8$:$Eu^{2+}$, were distinguished for promising PL intensity and improved color chromaticity. However, the PL and structural properties of all other compositions were also acceptable, with the exception of nonsingle-phase phosphors appearing in the Mg-rich area of the ternary library.

ASSOCIATED CONTENT

Supporting Information. Video showing the entire high-throughput process. This material is available free of charge via the Internet at http://pubs.acs.org.

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