Discovery of a Novel Nitride Phosphor by High Throughput Calculations

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ABSTRACT

Discovery of new phosphors with interesting properties is driven by rapid advances in lighting and displays. In this paper, we screened and searched for a super-broadband phosphor $Sr_2AlSi_2NO_6:Eu^{2+}$ by using high throughput calculations. The emission of the phosphor covered the whole range of the visible light, enabling to create super-high color rendition white light when pumped by a UV-LED chip.

1 INTRODUCTION

Inorganic luminescent materials play an indispensable role in phosphor-converted white light-emitting diodes (pc-wLEDs), which down-convert the emission of near UV- or blue LEDs into the visible light.[1] To achieve high quality white light (*i.e.*, high color rendering index and high luminous efficiency), it is required to carefully choose the phosphors. The method of "yellow/orange phosphor + blue LED" can produce high efficiency wLEDs but with a low color rendering index (Ra < 80) due to the lack of enough red or green spectral component, whereas the multi-phosphor option enables to yield high color rendition wLEDs but with a low efficiency owing to the re-absorption among different phosphors. To overcome the disadvantages of each approach, a super-broadband phosphor that has the emission covering the whole part of the visible light should be developed. Usually a broadband emission can be obtained in cases of (i) there are several crystallographic sites for luminescent centers in one host; (ii) there is structural disordering; and (iii) there is energy transfer between the same or different activators.

There are some approaches to screen and search for novel phosphors, including the traditional trial-and error method, single-crystal analysis,[2] combinatory chemistry,[3] single-particle-diagnosis,[4] structure unit substitution,[5] high throughput calculation[6] and machine learning.[7] Some promising phosphors, such as narrow-band phosphors and thermally stable phosphors, have been discovered for white LEDs or displays.[2,7]In this work, we tried to find a Eu^{2+}-activated full-visible-spectrum phosphorin the relatively unexplored system Sr-Al-Si-O-N by combining data mining of high-throughput density functional theory (DFT) calculations and experiments.This choice is guided by the hypothesis that the relatively similar ionic radii of the cations Al^{3+} and Si^{4+} as well as the anions N^{3-} and O^{2-}enable to produce disordered solid solution phases, then a broadband emission then can be expected.

2 EXPERIMENT

All density functional theory (DFT) calculations were performed using the Vienna *ab* initio simulation package (VASP) within the projector-augmented wave method.[8,9]The detailed information will be given in the presentation. The newly discovered phosphor powder of $Sr_2AlSi_2O_6N:Eu^{2+}$ was prepared by firing the powder mixture of $SrCO_3$, $CaCO_3$, Eu_2O_3, Si_3N_4, SiO_2 and Al_2O_3 at 1380ºC for 4h under N_2-10%H_2 atmosphere in a horizontal tube furnace, followed by sintering at 1400 ºC for 4h under a nitrogen pressure of 0.9 MPa in a gas pressure sintering furnace. The crystal structure and photoluminescence properties of the samples were characterized and discussed.

3 RESULTS AND DISCUSSION

Using a similar approach reported in a previous work,[6,11] we generated 496 novel candidate crystals in the Sr-Al-Si-O-N chemical space by applying data-mined ionic substitution on the database of ICSD-2017, and then a high-throughput DFT screening was done to identify the most promising phosphor hosts (see Fig. 1)

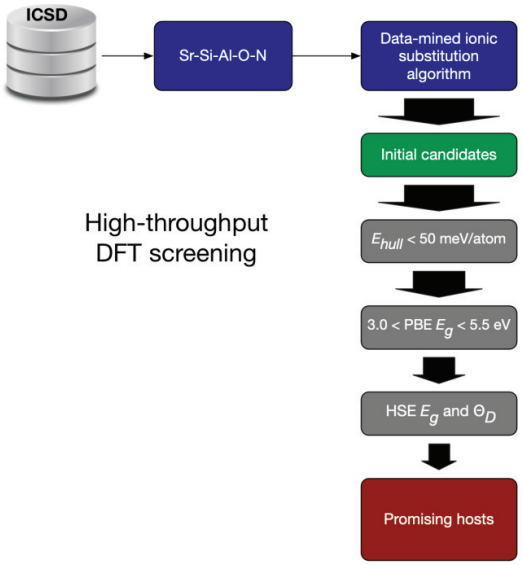

Figure 1. High throughput screening of promising broadband phosphors

By using the high throughput calculation we discovered $Sr_2AlSi_2O_6N$ as a new phosphor. Its crystal structure is isotypic to $Ba_2ZnGe_2S_6O$ (ICSD no. 14174) and exhibits alternating Sr and Si/Al layers with a single Sr crystallographic site, as shown in Fig. 2 (left). $Sr_2AlSi_2O_6N$ is both thermodynamically and dynamically stable by DFT computations, and the band gap is 3.82eV calculated using the Perdew-Burke-Ernzerhof (PBE) function.[12]Based on an approximate mean-field approach,we have constructed the anion-disordered structure model given in Fig. 2 (right) with Al located on the 2a site, Si on the 4e site and the uniformly disordered N/O.The disordered structure of $Sr_2AlSi_2O_6N$implies that the emission spectrum ofEu^{2+}would be broad.

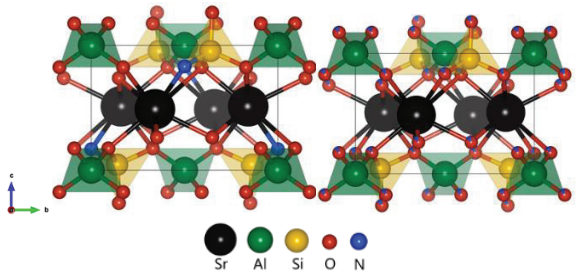

Figure 2 Unit cell of ordered (left) and anion disordered (right) $Sr_2AlSi_2O_6N$ structure

A phase pure $Sr_2AlSi_2O_6N$ powder was synthesized by using a two-step firing. The predicted crystal structure of $Sr_2AlSi_2O_6N$ was refined using the Rietveld analysis of the XRD profile (Fig. 3). The reliability factors are R_{wp}=6.10% and R_p =4.67%, respectively.

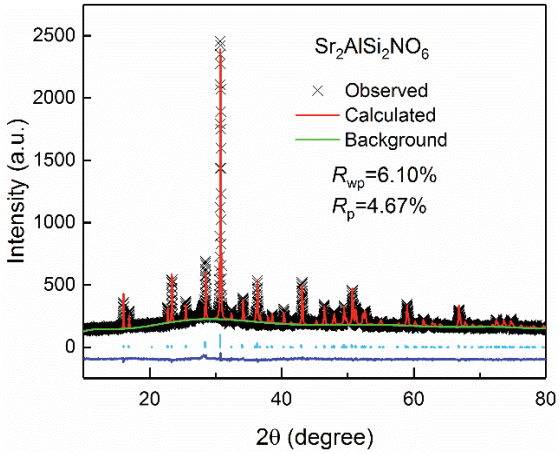

Figure 3 Rietveld refinement of $Sr_2AlSi_2NO_6$.

As seen in Fig.4, the $Sr_2AlSi_2O_6N:Eu^{2+}$ has a strong absorption at 330 nm. Under 330 nm excitation, the title phosphor shows a bright white light with chromaticity coordinates (0.4041,0.3851). The emission spectrum displays an extremely broadband with a maximum of 600 nm and a full-width at half maximum (FWHM) of 230 nm, covering the whole visible light region (400 – 850 nm).Such a large FWHM is hardly seen for Eu^{2+}. Since there is only one crystallographic site, the super-broadband emission is ascribed to the multiple local environments for Eu^{2+}as a result of the disordering of both Al/Si and O/N. It thus allows to create high color rendering white light by using a single phosphor, avoiding the reduction in luminous efficiency caused by re-absorption. By combining $Sr_2AlSi_2O_6N:Eu^{2+}$with a near UV-LED chip, a warm white LED was demonstrated. It shows a correlated color temperature (CCT) of ~3500 K and high color rendering indexes (Ra=96, R9=81).

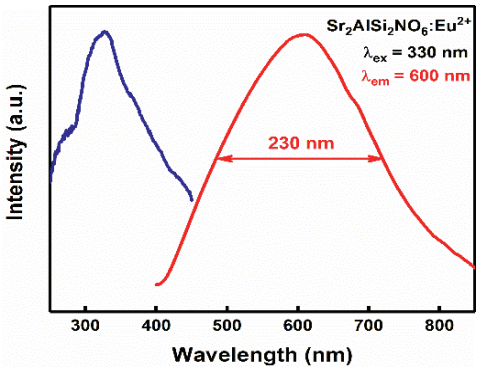

Figure 4 Photoluminescence spectra of $Sr_2AlSi_2NO_6:Eu^{2+}$. The left excitation spectrum was monitored at 600 nm and the right emission spectrum was measured under 330 nm excitation.

In addition, the quantum efficiency of $Sr_2AlSi_2NO_6:Eu^{2+}$isquite low, owing to the large Stokes shift. By substitution of Sr by Ca, an improvement in quantum efficiency is seen.

4 CONCLUSIONS

By DFT structure prediction and PL-related propertiescalculation, a novel super-broadband $Sr_2AlSi_2O_6N:Eu^{2+}$ phosphor was discovered. The newly discovered nitride host was isostructural to $Ba_2ZnGe_2S_6O$, and had structural disordering of both Si/Al and O/N. It showed a full-visible-spectrum emission with a FWHM of 230 nm and a thermal quenching temperature of 500 K.The warm white LED prepared by using only $Sr_2AlSi_2O_6N:Eu^{2+}$showed excellent color quality (Ra = 96, R9 = 81). The method in this work paves the way to rapidly discover new phosphors with promising properties.

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REFERENCES

[1] L. Wang, R.-J.Xie, T. Suehiro, T. TakedaandN. Hirosaki, “Down-Conversion Nitride Materials for Solid State Lighting: Recent Advances and

Perspectives," Chem. Rev., Vol. 118, pp. 1951-2009 (2018).
[2] P.Pust, V.Weiler, C. Hecht, A. Tucks, A.S. Wochnik, A.K. Henβ, D. Wiechert, C. Scheu, P.J. Schmidt and W.Schnick, "Narrow-BandRed-Emitting $Sr[LiAl_3N_4]:Eu^{2+}$ as a Next-Generation LED-Phosphor," Nat. Mater.,Vol. 13, 891−896 (2014).
[3] W.B. Park, N. Shin, K.P. Hong, M.Pyo and K.S. Sohn, "A NewParadigm for Materials Discovery: Heuristics-Assisted CombinatorialChemistry Involving Parameterization of Material Novelty,". Adv. Funct.Mater.,Vol. 22, 2258−2266 (2012).
[4] N.Hirosaki, T. Takeda, S.Funahashi andR.-J.Xie, "Discovery ofNew Nitridosilicate Phosphors for Solid State Lighting by the Single-Particle-Diagnosis Approach," Chem. Mater.,Vol. 26, 4280−4288 (2014).
[5] Z. Xia, C. Ma, M.S.Molokeev, Q. Liu, K. Rickert and K.R. Poeppelmeier, "Chemical Unit Cosubstitution and Tuning of Photoluminescence in the $Ca_2(Al_{1-x}Mg_x)(Al_{1-x}Si_{1+x})O_7:Eu^{2+}$ Phosphor," J. Am. Chem. Soc., Vol. 137, 12494-12497 (2015).
[6] Z. Wang, J. Ha, Y.H. Kim, W.B. Im, J. McKittrick and S.P. Ong, "Mining Unexplored Chemistries for Phosphors for High-Color-Quality White-Light-Emitting Diodes," Joule, Vol.2, 914-926 (2018).
[7] Y. Zhuo, A. M. Tehrani, A. O. Oliynyk, A. C. Duke, J. Brgoch, "Identifying an Efficient, Thermally Robust Inorganic Phosphor Host via Machine Learning," Nat. Commun., Vol. 9, 4377 (2018).
[8] G.Kresse and J.Furthmüller, "Efficient Iterative Schemes for ab initio Total-Energy Calculations Using a Plane-Wave Basis Set," Phys. Rev. B., Vol. 54, 11169-11186 (1996).
[9] P.E. Blöchl, "Projector Augmented-Wave Method," Phys. Rev. B., Vol. 50, 17953-17979 (1994).
[11] Z. Wang, I.-H. Chu, F. Zhou, Fand S.P. Ong, "Electronic Structure Descriptor for the Discovery of Narrow-Band Red-Emitting Phosphors," Chem. Mater., Vol. 28, 4024-4031 (2016).
[12] J.P. Perdew, K. Burke and M. Ernzerhof, "Generalized Gradient Approximation Made Simple," Phys. Rev. Lett., Vol. 77, 3865-3868 (1996).