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Mining Unexplored Chemistries for Phosphors for High-Color-Quality White-Light-Emitting Diodes



The discovery of new phosphors is key to the development of highly efficient and environmentally friendly LED-based lighting. By applying data-driven structure prediction and quantum mechanics-based screening on unexplored chemistries, we identified a novel, earth-abundant phosphor host, Sr_2LiAlO_4 , which was successfully synthesized and integrated into prototype LEDs with high color quality.

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HIGHLIGHTS

Data-driven prediction and screening identified Sr₂LiAlO₄ as promising phosphor host

 Sr_2LiAlO_4 is the first synthesized quaternary oxide in the Sr-Li-Al-O chemical space

Sr₂LiAlO₄:Eu²⁺/Ce³⁺ exhibits green-yellow/blue emission with good thermal stability

LEDs with Sr₂LiAlO₄:Eu²⁺/Ce³⁺ phosphors yield light with excellent color quality

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Mining Unexplored Chemistries for Phosphors for High-Color-Quality White-Light-Emitting Diodes

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SUMMARY

There is a critical need for new earth-abundant phosphors to enable next-generation, highly efficient solid-state lighting. Here we report the discovery of Sr₂LiAlO₄, the first known Sr-Li-Al-O quaternary crystal, via a carefully targeted data-driven structure prediction and screening effort using density functional theory calculations. Sr₂LiAlO₄ is predicted and experimentally confirmed to be a thermodynamically and thermally stable phosphor host that can be excited with near-UV/blue sources. The Eu²⁺- and Ce³⁺-activated Sr₂LiAlO₄ phosphors exhibit broad emissions at $\lambda_{max} \sim 512$ nm (green-yellow) and $\lambda_{max} \sim 434$ nm (blue), respectively, with excellent thermal quenching resistance of >88% intensity at 150°C. A prototype phosphor-converted white LED utilizing Sr₂LiAlO₄ based phosphors yields an excellent color-rendering index exceeding 90. Sr₂LiAlO₄ therefore exhibits great potential for industrial applications in low-cost, high-color-quality WLEDs.

INTRODUCTION

Phosphor-converted white-light-emitting diodes (pc-WLEDs) are among the most promising solid-state lighting (SSL) technologies due to their high energy efficiency and superior durability and reliability.^{1,2} For general illumination, we need a warm white light with excellent quantum efficiency, resistance to thermal quenching, and high color quality, i.e., a low color-correlated temperature (CCT) of <3,000 K and a high color-rendering index (CRI) of >85.³ Typical commercial WLEDs based on blue-emitting (~450 nm) LED chips combined with a yellow-emitting phosphor ($Y_3AI_5O_{12}:Ce^{3+}$) have poor CRI <80 and high CCT >5,000 K.⁴ To improve the CRI and CCT, an alternative approach is to use near-UV (380-420 nm) or blue LED chips with a mixture of red, green, and blue phosphors. Lu₃Al₅O₁₂:Ce³⁺ and (Ba,Sr)₂SiO₄:Eu²⁺ are two well-known green emitters with good photoluminescence (PL) properties used for these phosphor mixtures.⁵ Unfortunately, the former requires the rare-earth Lu in large quantities, while the latter suffers from severe thermal quenching. Meanwhile, most commercial red-emitters are Eu^{2+} -activated nitrides, such as CaAlSiN₃: Eu^{2+} and $Sr_2Si_5N_8$: Eu^{2+} , which are synthesized under harsh conditions (high temperature and high pressure).^{6,7} Yet another way to generate white light with high color quality is to leverage on a single-phase broad-band emitter that covers a wide range of the visible spectrum (400–700 nm). $Ba_{0.93}Eu_{0.07}Al_2O_4$ is an example of a recently discovered broad-band phosphor with good CRI >80 and CCT <4,000 K,⁸ but its synthesis requires a high temperature of 1,450°C and a low pressure of 667 Pa.

Context & Scale

Solid-state lighting based on phosphor-converted lightemitting diodes (pc-WLEDs) are highly efficient, environmentally friendly, and exhibit superior durability and reliability. For domestic lighting, a warm whitelight LED with good quantum efficiency, resistance to thermal quenching, high color-rendering index (CRI), and low correlated color temperature is desired. Here, we report the discovery of an earth-abundant Sr₂LiAlO₄ phosphor host using data-driven structure prediction and screening of unexplored chemistries. The synthesized Sr₂LiAlO₄:Eu²⁺ and Sr₂LiAlO₄:Ce³⁺ phosphors exhibit broad green-yellow and blue emissions, respectively, with excellent thermal quenching resistance. A prototype pc-WLED utilizing Sr₂LiAlO₄:Eu²⁺ yields an excellent CRI > 90. This work highlights the effectiveness of an integrated in silico and experimental approach in the discovery of a technological material in a novel chemistry.

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There is therefore an urgent need to discover novel earth-abundant phosphors with reasonably facile synthesis for pc-WLED applications. Hitherto, the discovery of phosphor materials has largely taken place through painstaking experiments, such as using exploratory crystal growth,¹ combinatorial chemistry screening,⁹ and single-particle diagnosis,¹⁰ in an Edisonian fashion. In recent years, high-throughput density functional theory (DFT) calculations have emerged as a powerful complementary tool to experiments to accelerate materials discovery, with successes having been demonstrated in many application areas.^{11–14} By enabling rapid evaluation across multiple application-specific properties, DFT calculations can be used to effectively screen thousands of materials to identify a small subset of candidates for subsequent synthesis and experimental evaluation. Nevertheless, there have been no successful demonstrations of *in silico* phosphor discovery to date, no doubt due in part to extensive experimental efforts in the field as well as the difficulty in predicting optical properties with DFT.

In this work, we report the discovery of a novel, earth-abundant phosphor host, Sr₂LiAlO₄, which to the authors' knowledge is also the first known Sr-Li-Al-O quaternary compound. Sr₂LiAlO₄ was identified via a carefully targeted data-driven structure prediction and DFT screening effort guided by statistical analysis of known phosphors in the Inorganic Crystal Structure Database (ICSD).¹⁵ We demonstrate that Sr₂LiAlO₄ is predicted by DFT calculations to be thermodynamically and dynamically stable and to have the necessary bandgap, structural rigidity, and near-UV excitation wavelength when activated with either Eu²⁺ or Ce³⁺. High-purity Sr₂LiAlO₄ was synthesized via industrially scalable methods and characterized using X-ray diffraction (XRD) and photoluminescence spectroscopy. The Eu²⁺ and Ce³⁺ activated Sr₂LiAlO₄ phosphors exhibit broad emissions of $\lambda_{max} \sim 512$ nm (greenyellow) and $\lambda_{max} \sim 434$ nm (blue), respectively, with excellent thermal quenching resistance of >88% intensity at 150°C. A prototype pc-WLED utilizing Sr₂LiAlO₄:Eu²⁺ yields an excellent CRI of >90.

RESULTS AND DISCUSSION

Data-Driven Discovery of New Phosphors

We began our search for novel phosphor hosts by constructing a "solid-state lighting" periodic table (Figure 1A) from a statistical analysis of all compounds in the 2017 version of the ICSD with the word "phosphor" in the publication title. The high frequency of elements N, S, F, and Cl can be ascribed to the fact that (oxy) nitrides, (oxy)halides, and sulfides are some of the most well-studied phosphor materials.^{16–18} Nevertheless, oxides are overwhelmingly preferred in practical SSL applications due to their typically more facile synthesis and better chemical stability under ambient conditions; therefore, these other anion types will not be further considered in this work. We may observe a preponderance of the alkalineearth metals (Mg/Ca/Sr/Ba), alkali metals (Li/Na/K), and main group elements (Al/Si/P/B) among known phosphors. The presence of Ca and Sr is not surprising, given that the ionic radii of Ca^{2+} and Sr^{2+} are similar to those of the common Ce^{3+} and Eu²⁺ activators.¹⁹ Na⁺ also presents a high frequency in phosphor hosts due to its similar size to Eu²⁺. However, activation via aliovalent substitution of Na⁺ by Eu²⁺ would require the identification of the most stable charge-compensating defect and the use of large-supercell DFT calculations. Therefore, we have chosen to focus on systems containing $Sr^{2+}/Ba^{2+}/Ca^{2+}$ in this work as these are isovalent with Eu²⁺. Given that phosphates, silicates, aluminates, and borates are among the most commonly studied oxides in SSL,¹⁶⁻¹⁸ we then proceeded to identify

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Figure 1. Data-Driven Discovery of Sr₂LiAlO₄

(A) Frequency at which each element appears in compounds having the word "phosphor" in the publication title in the 2017 version of ICSD. Only nonrare-earth elements are shown. Elements with frequency 0 are shaded in gray.

(B) Calculated 0 K SrO-Li₂O-Al₂O₃ phase diagram. Blue circles, known stable phases in the Materials Project database; red square, new stable quaternary phase, Sr_2LiAlO_4 .

(C) Unit cell of the Sr₂LiAlO₄ (P2₁/m) crystal and the two symmetrically distinct Sr sites. Numbers indicate Sr-O bond lengths in angstroms.

opportune chemistries for novel phosphor host discovery in the ternary M-X-O (M = Ba/Sr/Ca, X = P/Si/Al/B) and quaternary M-L-X-O (M = Ba/Sr/Ca, L = Li/Mg/Y, X = P/Si/Al/B) oxides.

We find that while ternary M-X-O oxides have been relatively well explored, significant opportunities exist in quaternary M-L-X-O oxides. In particular, there are no reported compounds in the ICSD in seven chemistries: Ba/Sr/Ca-Li-Al-O, Sr-Li-P-O, Ba/Sr-Y-P-O, and Ba-Y-Al-O (Figure S1). A further search of the larger Pauling File database²⁰ turned up one known compound each in the Sr-Li-P-O, Ba/Sr-Y-P-O, and Ba-Y-Al-O chemistries, and still no compounds in the Ba/Sr/Ca-Li-Al-O chemistries. We generated 918 new crystal structure candidates in these seven unexplored chemical systems by applying a data-mined ionic substitution algorithm²¹ on the entire ICSD (see Experimental Procedures). These candidates were then systematically evaluated via an efficiently tiered series of DFT property calculations (Figure S2). The first criterion that any technological material must satisfy is synthesizability and stability. Thermodynamic stability is estimated by calculating the energy above the linear combination of stable phases in the 0 K DFT phase diagram, also known as E_{hull} . A typical threshold for synthesizability used in previous DFT

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screening works is an E_{hull} of <30–50 meV per atom.^{13,22} We find that the four known phosphors in the Sr-Li-P-O, Ba/Sr-Y-P-O, and Ba-Y-Al-O chemistries reported in the Pauling database are indeed among the candidates generated by the structure prediction algorithm, and all four compounds have a calculated E_{hull} < 35 meV per atom (Table S1). The successful prediction of these "unseen" known phosphors from the ICSD gives us confidence that viable candidates are identified via the combination of the data-mined ionic substitution algorithm and DFT calculations. Among the remaining Ba/Sr/Ca-Li-Al-O chemical systems with no known compounds, we will focus primarily on the Sr-Li-Al-O chemistry due the fact that Sr²⁺ has an ionic radius (1.26 Å) that is closest to Eu²⁺ (1.25 Å), compared with Ba²⁺(1.42 Å) or Ca²⁺(1.12 Å).¹⁹ Also, Li and Al are inexpensive, earth-abundant elements that tend to form rigid bonds in crystals.

Figure 1B shows the calculated 0 K SrO-Li₂O-Al₂O₃ phase diagram. We find that one of the new candidates, Sr₂LiAlO₄, is predicted to be thermodynamically stable ($E_{hull} = 0$). The computed phonon spectrum (Figure S3) confirms it to be also dynamically stable. The crystal structure of Sr₂LiAlO₄ (space group: $P2_1/m$) is shown in Figure 1C, and the structural parameters are provided in Table S2. Sr₂LiAlO₄ is derived from Ba₂LiReN₄ (ICSD no. 411453) via a multi-species substitution of Ba²⁺ with Sr²⁺, Re⁷⁺ with Al³⁺, and N³⁻ with O²⁻. This is clearly a non-trivial crystal prediction that cannot be easily replicated using traditional chemical intuition.

We evaluated the potential PL properties of the stable Sr₂LiAlO₄ host by calculating its electronic structure and Debye temperature (Θ_D). The calculated bandgap E_g of Sr₂LiAlO₄ using the Perdew-Burke-Ernzerhof (PBE) functional¹³ is 4.19 eV, which suggests that it would yield a green-yellow emission with Eu²⁺ activation based on the inverse relationship between experimental wavelength and the PBE E_g previously reported by the current authors.¹³ In general, host materials that have a large photoionization barrier, defined as the energy gap between conduction band minimum and excited 5*d* level, are rigid and tend to exhibit excellent thermal quenching resistance.^{23,24} The calculated bandgaps of Sr₂LiAlO₄ using the more accurate Heyd-Scuseria-Ernzerhof (HSE)^{25,26} functional and $G_0W_0^{27}$ are 5.91 eV and 6.00 eV, respectively. This large bandgap suggests a strong likelihood of a large photoionization barrier. The calculated Θ_D of Sr₂LiAlO₄ is 466 K, indicating that it has a rigid crystal structure.²⁸

There are two symmetrically distinct Sr crystallographic sites (labeled Sr1 and Sr2 in Figure 1C) in Sr₂LiAlO₄, both of which are 8-fold coordinated with oxygen atoms. By performing an isovalent substitution a single Eu^{2+} into a 2 × 2 × 2 supercell of Sr_2LiAlO_4 (16 formula units), we determined using DFT calculations that the Eu²⁺ activator prefers the Sr1 site to the Sr2 site by about 35 meV. For Ce³⁺ activation, we comprehensively evaluated various charge-neutral defect configurations, taking into account typical experimental synthesis conditions such as excess Li from its volatility at elevated temperature. We find that the $2Ce_{sr}^{\cdot} + Li_{Al}^{\prime\prime}$ defect combination (Kröger-Vink notation) has the lowest defect formation energy compared with $2Ce_{Sr}^{\cdot}+V_{Sr}^{\prime\prime}$ (0.22 eV/Ce^{3+} higher) and Ce_{Sr}^{\cdot}+Li_{Sr}^{\prime} (1.48 eV/Ce^{3+} higher). Hence, we conclude that the substitution of Ce^{3+} on Sr^{2+} is likely to be charge compensated by excess Li⁺ on the Al³⁺ tetrahedra, as opposed to vacancy formation or excess Li⁺ on the Sr²⁺ site. This is consistent with the fact that the small Li⁺ ion (ionic radius = 0.9 Å) is likely to prefer the AlO₄ tetrahedron rather than the much larger SrO_8 site. Henceforth, we will use the shorthand notation commonly used in the phosphor community, Sr₂LiAlO₄:xEu²⁺ and Sr₂LiAlO₄:yCe³⁺, to denote the activated structures with compositions $Sr_{2-x}Eu_xLiAIO_4$ and $Sr_{2-y}Ce_yLi_{1+y/2}AI_{1-y/2}O_4$, respectively.

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All subsequent DFT results on activated hosts, unless otherwise stated, were performed using the configuration with the lowest defect formation energy.

For efficient conversion, a phosphor should have absorption spectrum peaking at the maximum emission of LED chips. The absorption spectra for Sr₂LiAlO₄:0.0625Eu²⁺ and Sr₂LiAlO₄:0.125Ce³⁺ were calculated using the Bethe-Salpeter equation (BSE) method²⁹ on top of G_0W_0 , as shown in Figure 2. For both activated phosphors, the main absorption peaks are observed at 380–420 nm, which can be attributed to $4f^7 \rightarrow 4f^65d^1$ transition in Eu²⁺ or $4f^1 \rightarrow 4f^05d^1$ transition in Ce³⁺. These findings suggest that both Eu²⁺ and Ce³⁺-activated Sr₂LiAlO₄ can be efficiently excited by near-UV LED chips.

Synthesis and Photoluminescence Properties

The Sr₂LiAlO₄ host and the Eu²⁺- and Ce³⁺-activated phosphors were successfully produced using solid-state reaction as well as combustion synthesis. Here, we will discuss primarily the results from the samples synthesized via solid-state reaction, given that this is the preferred approach in commercial applications due to its low cost, availability of precursors, and potential for production on an industrial scale. In general, other than a higher purity (94% versus 86% for solid-state reaction), the measured structural parameters and PL properties of the combustion-synthesized samples are very similar. Figure 3 shows the simulated and measured XRD profiles of the host and activated phosphors, which are in excellent agreement and confirm the successful synthesis of the predicted Sr₂LiAlO₄ compound. The residual factors of Rietveld refinement analysis of the XRD profile (see Table S3) are $R_{wp} = 9.11\%$, $R_p = 6.69\%$, and goodness of fit (GOF) = 2.79. The refined structure parameters are also in excellent agreement with those from the DFT relaxed structure (see Tables S2 and S3).

The measured PL spectrum of the Sr_2LiAlO_4 :0.005Eu²⁺ phosphor excited at 394 nm (Figure 4A) shows a green-yellow emission peaking at 512 nm with a shoulder peak of 559 nm. The emission spectrum is broad (full width at half maximum [FWHM] = 73.6 nm) and asymmetric, indicating that Eu²⁺ ions occupy two distinct sites in the Sr_2LiAlO_4 host. The excitation spectrum monitored at 512 nm shows a broad band with two main peaks at 310 nm and 394 nm. The PL spectrum of the Sr_2LiAlO_4 :0.005Ce³⁺ phosphor measured at 384 nm excitation (Figure 4B) shows a broad blue emission with a main peak at 434 nm and an FWHM of 70.3 nm. The PL excitation recorded at 434 nm also presents two peaks: one major peak at

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Figure 3. Simulated and Measured X-Ray Diffraction Patterns of Sr_2LiAlO₄, Sr_2LiAlO₄:0.005Eu²⁺, and Sr_2LiAlO₄:0.005Ce³⁺

384 nm and one minor peak at 291 nm. The measured excitation spectra are consistent with the 4f-5d transitions of Eu²⁺/Ce³⁺ ions, and the BSE-computed excitation wavelengths in Figure 2.

A careful optimization of the PL properties of Sr₂LiAlO₄:xEu²⁺ and Sr₂LiAlO₄:yCe³⁺ was carried out with respect to activator concentration (*x*, *y*). As shown in Figure 4C, the emission intensity slightly increases and then decreases with increasing activator concentration, with the maximum emission intensity occurring at *x* or *y* = 0.005 for both activators. The measured internal quantum efficiencies of the Sr₂LiAlO₄:0.005Eu²⁺ and Sr₂LiAlO₄:0.005Ce³⁺ phosphors are 25% (λ_{ex} = 394 nm) and 32% (λ_{ex} = 392 nm), respectively.

Figure S4 presents the unnormalized and normalized PL spectra of Sr₂LiAlO₄:xEu²⁺ with respect to a series of Eu²⁺ concentrations (0.0025 $\leq x \leq$ 0.0500) measured at room temperature. With increasing Eu²⁺ concentration, the relative intensity of short excitation wavelength (at 320 nm) gradually decreases, while the relative intensity of long wavelength (at 480 nm) slightly increases, as shown in Figure S4C. At the same time, a corresponding increase of emission intensity at 559 nm is also observed with increasing of Eu²⁺ concentration when normalized based on emission intensity at 512 nm, as shown in Figure S4D. We believe the lower energy emission (longer wavelength) peaks are associated with more Eu²⁺ occupying the energetically more favorable Sr1 site. The calculated average bond length (I_{av}) of EuO₈ polyhedron in the Sr1 site and Sr2 site are 0.269 nm and 0.272 nm, respectively, while the distortion indices (D) (see Experimental Procedures for definitions) are 0.056 and 0.044, respectively. A shorter I_{av} and larger D is associated with a larger crystal field splitting (CFS).^{30,31} The larger CFS of Eu²⁺ in the Sr1 site leads to a red shift in emission, as illustrated in Figure 4D. These conclusions are further supported by deconvolution of the PL emission spectra of Sr₂LiAlO₄:0.005Eu²⁺ at 10 K and 298 K (Figures S5A and S5B), which shows a significant decrease in the long wavelength emission at room temperature. The lower thermal stability of the Eu in the Sr1 site

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(D) Schematic energy level diagram for Eu^{2+}/Ce^{3+} ions in the Sr_2LiAlO_4 host crystal structure. ΔE_{ne} and ε_{cfs} denote the centroid shift due to the nephelauxetic effect and the crystal field splitting of Eu^{2+}/Ce^{3+} ions in the Sr_2LiAlO_4 host, respectively. ΔE_A is the photoionization barrier.

is also a consequence of its larger CFS, which leads to a smaller barrier for photoionization (ΔE_A).²³ To obtain further support for these conclusions, we calculated the HSE projected density of states (Figure S6) for a Sr₂LiAlO₄:Eu²⁺ structure where Eu is introduced into both Sr1 and Sr2 simultaneously. We find that Eu in the Sr1 site has a smaller gap (longer excitation wavelength) between the 4f and 5d states compared with Eu in the Sr2 site.

In contrast, there are no significant changes in the relative intensities of both the excitation and emission peaks at different wavelengths with increasing of Ce^{3+} concentration in $Sr_2LiAlO_4:yCe^3$ (Figure S7). The emission spectra of $Sr_2LiAlO_4:0.005Ce^{3+}$ can be deconvoluted into four Gaussian peaks at 10 K with position of 433 (peak 1: 23,095 cm⁻¹), 468 (peak 2: 21,368 cm⁻¹), 497 (peak 3: 20,121 cm⁻¹), and 532 nm (peak 4: 18,797 cm⁻¹), as shown in Figure S5C. The energy difference between peak 1 and peak 3 is about ~2,974 cm⁻¹ (0.37 eV), and between peak 2 and peak 4 is about ~2,571 cm⁻¹ (0.32 eV). These values correspond to the spin-orbit splitting energy of the lowest 4f level (${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$) in Ce^{3+} .³² However, at 298 K (Figure S5D) only two Gaussian peaks are observed at 427 nm (23,419 cm⁻¹) and 460 nm (21,739 cm⁻¹). These observations again suggest that the Sr1 site, associated with the long wavelength emission, is thermally unstable with no PL at room temperature.

Thermal Stability

In practical applications, WLEDs typically operate at elevated temperatures (~150°C), and a key metric of phosphor performance is its resistance to thermal quenching. Figure 5 shows the measured temperature-dependent emission intensity for Sr₂LiAlO₄:0.005Eu²⁺. At 150°C, the emission intensity of the main peak

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Figure 5. Thermal Quenching and Site-Dependent Photoluminescence Properties of Sr_LiAlO_4:0.005Eu $^{2+}$

(A) Temperature-dependent emission spectra under 394 nm excitation in the temperature range of 25° -200°C.

(B) Normalized temperature-dependent emission intensity under the peak emission wavelength (λ_{max}), 559 nm and integrated emission intensity (total area) with a temperature interval of 25°C.

 $(\lambda_{em} \sim 512 \text{ nm})$ is about 88% of that at room temperature. The emission intensity of the secondary peak ($\lambda_{em} \sim 559 \text{ nm}$), which is associated with Eu²⁺ in the thermally less stable Sr1 site, on the other hand, reduces significantly with increasing temperature. Overall, Sr₂LiAlO₄:0.005Eu²⁺ exhibits excellent resistance to thermal quenching. The Sr₂LiAlO₄:0.005Ce³⁺ phosphor is found to have a slightly better resistance to thermal quenching, retaining 91% of room temperature peak emission intensity at 150°C (Figure S8).

Performance of WLEDs

Finally, we constructed prototype WLED devices using Sr₂LiAlO₄:Eu²⁺ and Sr₂LiAlO₄:Ce³⁺ as well as a mixture of Sr₂LiAlO₄:Eu²⁺/Ce³⁺. The electroluminescence (EL) spectra of these WLEDs are shown in Figures 6A-6C. The prototype WLED using Sr₂LiAlO₄:Eu²⁺ exhibits CIE color coordinates of 0.301 and 0.323, with high CRI of 93 and a CCT of 7,527 K at a forward bias current of 60 mA (Table S4). The excellent CRI of the Sr₂LiAlO₄:Eu²⁺ phosphor can be attributed to the feature of its broad-band emission by two Sr sites. The CCT of the WLED can be further lowered by using a mixture of Sr₂LiAlO₄:Eu²⁺/Ce³⁺, as shown in Table S5, as well as via the addition of a red component. For instance, the recently reported SrLiAl₃N₄:Eu²⁺ narrow-band red phosphor¹ would be a particularly interesting option, which would allow for the construction of an oxide + nitride device using the same earth-abundant elements. The measured luminous efficacy of WLEDs with Sr_2LiAlO_4 : Eu^{2+}/Ce^{3+} phosphors are 19–36 lm W⁻¹, which is comparable with that of WLEDs utilizing some recently reported novel phosphors, but still somewhat lower than that of commercial WLEDs utilizing the Y₃Al₅O₁₂:Ce³⁺ phosphor (Table S6). To further improve the quantum efficiency of Sr₂LiAlO₄, crystal-site engineering techniques,^{17,33} e.g., co-doping with Ba or Ca, may be used to shift the energetic preference and/or tune the CFS of the two Sr sites.

To conclude, we have identified a novel earth-abundant Sr_2LiAlO_4 phosphor host the first known Sr-Li-Al-O quaternary compound—by composing a "solid-state lighting" periodic table based on statistical analysis of the ICSD to identify unexplored yet promising chemical spaces with data-mined structure prediction and highthroughput DFT property computations. Sr_2LiAlO_4 comprises inexpensive, earthabundant elements (other than the rare-earth activator, which is required in small quantities), and the DFT and PL results show Sr_2LiAlO_4 :Eu²⁺/Ce³⁺ to have efficient near-UV excitation, good thermal quenching resistance, and broad green-yellow/ blue emission. High-purity Sr_2LiAlO_4 -based phosphors can be synthesized with



Figure 6. Performance of Prototype pc-WLED Using the Single Sr₂LiAlO₄:Ce³⁺ and Sr₂LiAlO₄:Eu²⁺ Phosphor

(A) Electroluminescence (EL) spectra and photograph of the InGaN LED ($\lambda_{max} = 400 \text{ nm}$) + Sr₂LiAlO₄:0.005Ce³⁺ phosphor. (B) EL spectra and photograph of the InGaN LED ($\lambda_{max} = 400 \text{ nm}$) + Sr₂LiAlO₄:0.005Ce³⁺ + Sr₂LiAlO₄:0.005Eu²⁺ phosphor.

(C) EL spectra and photograph of the InGaN LED (λ_{max} = 450 nm) + Sr₂LiAlO₄:0.005Eu²⁺ phosphor.

(D) Photograph of WLEDs packaged with Sr_2LiAlO_4 :0.005Eu²⁺ phosphor.

(E) CIE chromaticity coordinates of the fabricated Sr₂LiAIO₄-based phosphors WLED under various forward bias currents.

scalable, industrially relevant methods. We therefore believe the novel Sr₂LiAlO₄:Eu²⁺/Ce³⁺ phosphors to be highly promising candidates for low-cost, high-CRI WLED applications.

EXPERIMENTAL PROCEDURES

Candidate Structure Generation

New crystal structure candidates for the target chemistries were generated by applying a retrained version of the ionic substitution algorithm developed by Hautier et al.²¹ on the ICSD.¹⁵ This algorithm codifies data-mined probabilities for substitution of one species by another. New candidates are generated by performing high-probability substitutions on a list of known crystal structures, in this case all ordered crystal structures in the 2017 version of the ICSD.

Density Functional Theory Calculations

All DFT calculations were carried out using the Vienna *ab initio* simulation package, VASP, within the projector-augmented wave method.^{34,35} The generalized gradient approximation PBE functional³⁶ was used for structural relaxations and energy calculations. The plane wave energy cutoff was 520 eV, and the Brillouin zone was integrated with a *k*-point grid at least of 100 per Å⁻³ (reciprocal lattice volume). All host crystal structures were relaxed with parameters in line with Materials Project.³⁷ The Eu²⁺/Ce³⁺-activated phosphor structures were fully relaxed until the energies and forces were converged to 10⁻⁵ eV and 0.01 eV Å⁻¹, respectively. All crystal

structure manipulations and data analysis were carried out using the Python Materials Genomics package.³⁸

The phase stabilities of the predicted Sr-Li-Al-O compounds were estimated by calculating the energy above the linear combination of stable phases in the 0 K DFT phase diagram,³⁹ also known as the energy above hull, E_{hull} . Previous studies have shown that ~60% of ICSD oxides have E_{hull} less than 30 meV per atom;²² we therefore use this threshold as a reasonable cutoff for synthesizability. For phase diagram construction, the energies of all compounds other than those of direct interest in this work were obtained from the Materials Project³⁷ via the Materials Application Programming Interface.⁴⁰ The dynamical stability of the identified Sr₂LiAlO₄ host was evaluated by computing the phonon spectrum using density functional perturbation theory as implemented in the Phonopy code⁴¹ in conjunction with VASP³⁴ as the force calculator. More stringent energy and force criteria of 10⁻⁸ eV and 10⁻⁴ eV Å⁻¹, respectively, were used for these calculations.

Defect formation energies were calculated using the formalism presented by Wei et al.⁴²:

$$E_f = E_{tot}^D - E_{tot}^B - \sum_i n_i \mu_i,$$

where E_{tot}^D and E_{tot}^B are the total energies of the structure with and without the defect(s), respectively; μ_i is the atomic chemical potential of species *i*; n_i indicates the number of atoms of species *i* being added ($n_i > 0$) or removed ($n_i < 0$) to form the defect. μ_i is estimated based on the chemical pontentials for each specie based on the relevant region of the 0 K DFT phase diagram.

The host bandgaps were calculated using PBE for the initial rapid screening, and more detailed investigations of the electronic structure of Sr₂LiAlO₄ were carried out using the more computationally expensive and accurate screened hybrid HSE functional^{25,26} and single-shot *GW* method.²⁷ The BSE²⁹ simulation was performed on top of G_0W_0 to calculate the absorption spectrum of Eu²⁺/Ce³⁺-activated Sr₂LiAlO₄ phosphors. A large-supercell model (2 × 2 × 2, 128 atoms) was adopted to mimic the relatively low Eu²⁺/Ce³⁺ concentrations in the experiment and to avoid interactions between periodic images of activators.

The Debye temperature, Θ_D , was evaluated using the quasi-harmonic model. The elastic tensor was calculated with more stringent electronic convergence criterion of 10^{-6} eV, and the elastic moduli were calculated using the Voigt-Reuss-Hill approximation.^{13,43}

Local Environment Analysis

The local environment of the Eu²⁺ activator was characterized using the average Eu-O bond length (l_{av}) and the distortion index (*D*) of the EuO₈ coordination polyhedron. As per previous works, ^{30,31} *D* is defined as $D = \frac{1}{n} \sum_{i=1}^{n} \frac{|l_i - l_{av}|}{l_{av}}$, where l_i is the distance from the center atom to the *i*th coordinating atom, and *n* is the total number of Eu-O bonds (*n* = 8 in this case).

Synthesis

Solid-state reaction synthesis was performed using SrO (Kojundo, 99.9%), Li_2CO_3 (Kojundo, 99.9%), α -Al₂O₃ (Kojundo, 99.9%), and Eu_2O_3 (Kojundo, 99.9%) or CeO₂ (Kojundo, 99.99%). Stoichiometric amounts of the starting materials were ground in agate mortar, placed in alumina crucibles, and fired at 900°C for 4 hr in

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a horizontal tube furnace using a 25% H₂/N₂ gas mixture to obtain Sr₂LiAlO₄:xEu²⁺ and Sr₂LiAlO₄:yCe³⁺ (0.0025 \leq x, y \leq 0.0500). After heat treatment, the samples were cooled to room temperature and ground well with agate mortar into fine powders for further analysis. Excess Li source of up to 10 wt% was introduced to compensate for Li evaporation during synthesis.

Combustion reaction synthesis was performed using $Sr_2(NO_3)_2$ (99.99%, Sigma Aldrich), LiNO₃ (ReagentPlus, Sigma Aldrich), Al(NO₃)₃•9H₂O (ACS reagent, J.T. Baker), Eu(NO₃)₃ from Eu₂O₃ (99.99%, Alfa Aesar) with nitric acid (69.3%, Fisher Scientific), and Ce(NO₃)₃ (99.99%, Alfa Aesar) as precursors, assisted by the exothermal reaction between urea (Certified ACS, Fisher Scientific) and ammonium hydroxide (Certified ACS, Fisher Scientific) at 600°C. A post-annealing condition was 800°C for 5 hr in a 5% H₂/95% N₂ atmosphere to transform Eu³⁺ to Eu²⁺ to obtain Sr₂LiAlO₄:xEu²⁺ and Sr₂LiAlO₄:yCe³⁺ (0.001 \leq x, y \leq 0.040). Excess Li source of up to 25 wt% was introduced to compensate for Li sublimation during synthesis.

Crystal Structure Characterization

The powders by combustion reaction were analyzed by an X-ray diffractometer (Bruker D2 Phaser, Karlsruhe, Germany) using CuK α radiation and a step size of 0.014° over a 2 θ range of 20°–80°. XRD data of powders by solid-state reaction were obtained using CuK α radiation (Philips X'Pert). XRD data were collected over angles of 10° $\leq 2\theta \leq 120°$ with a step size of 0.026°. Structural information of the synthesized samples was derived by refinement using the TOPAS software suite from the XRD result. The VESTA program⁴⁴ was used to draw the crystal structure.

Optical Measurements

Photoluminescence of the solid-state-reaction synthesized samples was measured using a Hitachi F-4500 fluorescence spectrophotometer over a wavelength range of 200–700 nm. The quantum yield was measured with 394 nm and 450 nm excitation using a xenon laser (Hamamatsu C9920-02) at the Korea Photonics Technology Institute (KOPTI), Gwangju, South Korea. The thermal quenching characteristics were measured in the temperature range of 25° – 200° C, connected to the Hitachi F-4500 fluorescence spectrophotometer with integrated heater, temperature controller, and thermal sensor. Low-temperature PL spectra were obtained under excitation at 325 nm He-Cd laser connected to the cryostat system at the temperature of 10 K in the KOPTI.

Fabrication of pc-WLED Prototype

The white LED device prototype was fabricated by integrating the Sr₂LiAlO₄:0.005Ce³⁺ and mixed Sr₂LiAlO₄:0.005Ce³⁺/Eu²⁺ phosphors on an InGaN near-UV LED chip ($\lambda_{max} = 400$ nm) and the Sr₂LiAlO₄:0.005Eu²⁺ phosphor on an InGaN blue LED chip ($\lambda_{max} = 450$ nm). The device was then encapsulated in a phosphor/silicon resin mixture, with the mixture placed directly on the headers of LED chip and cured at 150°C for 1 hr. After the packaging was completed, the WLED device was measured in an integrating sphere under direct current forward bias condition.

SUPPLEMENTAL INFORMATION

Supplemental Information includes eight figures and six tables and can be found with this article online at https://doi.org/10.1016/j.joule.2018.01.015.

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AUTHOR CONTRIBUTIONS

Conceptualization, S.P.O. and Z.W.; Methodology, Z.W.; Investigation, Z.W., J.H., and Y.H.K.; Writing – Original Draft, Z.W., J.H., and Y.H.K.; Writing – Review and Editing, S.P.O., J.M., and W.B.I.; Supervision, S.P.O., J.M., and W.B.I.; Funding Acquisition, S.P.O., J.M., and W.B.I.

DECLARATION OF INTERESTS

A US provisional patent application Serial No. 62/572,084 has been filed on the novel phosphors reported in this work.

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