Systematic Approach To Calculate the Band Gap Energy of a Disordered Compound with a Low Symmetry and Large Cell Size via Density Functional Theory

Woon Bae Park,†,‡ Sung Un Hong,†,‡ Satendra Pal Singh, † Myoungho Pyo, ‡ and Kee-Sun Sohn*†

†Nanotechnology & Advanced Materials Engineering, Sejong University, 209 Neungdong-ro, Gwangjin-gu, Seoul 143-747, South Korea
‡Department of Printed Electronics, Sunchon National University, 291-19 Jungang-gyo, Sunchon, Chonnam 540-742, South Korea

Supporting Information

ABSTRACT: An ab initio calculation based on density functional theory (DFT) was used to verify the disordered structure of a novel oxynitride phosphor host, La_{4−x}Ca_{x}Si_{12}O_{33}N_{18−x}, with a large unit cell (74 atoms), low level of symmetry (C2), and large band gap (4.45 eV). Several Wyckoff sites in the La_{4−x}Ca_{x}Si_{12}O_{33}N_{18−x} structure were randomly shared by La/Ca and O/N ions. This type of structure is referred to as either partially occupied or disordered. The adoption of a supercell that is sufficiently large along with an infinite variety of ensemble configurations to simulate such a random distribution in a partially occupied structure would be an option that could achieve a reliable DFT calculation, but this would increase the calculation expenses significantly. We chose 5184 independent unit cell configurations to be used as input model structures for DFT calculations, which is a reduction from a possible total of 20,736 unit cell configurations for C2 symmetry. Instead of calculating the total energy as well as the band gap energy for all 5184 configurations, we pinpointed configurations that would exhibit a band gap that approximated the actual value by employing an elitist nondominated sorting genetic algorithm (NSGA-II) wherein the 5184 configurations were represented mathematically as genomes and the calculated total and band gap energies were represented as objective (fitness) functions. This preliminary screening based on NSGA-II was completed using a generalized gradient approximation (GGA), and thereafter, we executed a hybrid functional calculation (HSE06) for only the most plausible GGA-relaxed configurations with higher band gap energies and lower total energies. Finally, we averaged the HSE06 band gap energy over these selected configurations using the Boltzmann energy distribution and achieved a realistic band gap energy that more closely approximated the experimental measurement.

1. INTRODUCTION

We recently used a conventional solid-state combinatorial search process in association with metaheuristics strategies to screen a large selection of oxynitrides in an attempt to reveal novel phosphors that could be used in white-light-emitting diode (LED) applications.1−3 As a result, we discovered La_{4−x}Ca_{x}Si_{12}O_{33}N_{18−x}Eu^{2+} phosphors, which will be referred to as LCSON. The crystal structure of LCSON existed in none of the existing structure types listed in the Inorganic Crystal Structure Database (ICSD) and was determined to be monoclinic in the C2 space group, with the following lattice parameters: a = 18.54268(4), b = 4.840398(11), c = 10.700719(18), β = 108.25660(17), and the number of formula units per cell (z) = 2 (ICSD: 248802). The luminous intensity, reliability, and thermal stability of LCSON were comparable to those of the well-known commercially available yttrium aluminium garnet phosphors, as shown in Figure S1, which is available in the Supporting Information. Aside from the pragmatically successful functional performance of the material, a theoretical understanding of this phosphor is also of great interest.4,5

There have recently been a growing number of reports regarding density functional theory (DFT) calculations for luminescent materials for use in LEDs6−10 to understand their electronic structure and crystal stability. In this regard, the present investigation was focused on DFT calculations to theoretically validate the discovery of the novel structure, La_{4−x}Ca_{x}Si_{12}O_{33}N_{18−x}. A typical x value is around 1.5 and is based on the Rietveld refinement of a synchrotron light source X-ray diffraction (XRD) pattern and a neutron diffraction pattern.11−13 Using this x value in a feasible input model for DFT calculations would require special consideration due to the random distribution of La/Ca and O/N ions. This sort of structure is referred to as either disordered or partially occupied. In particular, disordered structures are frequently

DOI: 10.1021/acsomega.6b00190
ACS Omega 2016, 1, 483−490

Received: August 15, 2016
Accepted: September 16, 2016
Published: September 27, 2016
observed in many luminescent materials for use in LED applications, such as (Sr,Ba)SiN$_2$(O,N)$_x$ and CaAlSiN$_3$. In addition to the intrinsic disordered structures, the same disorder problem arises if either a doping or an elemental substitution is of concern. In this context, we ruled out the Eu$^{2+}$ disorder problem arises if either a doping or an elemental addition to the intrinsic disordered structures, the same dominant: virtual crystal approximation (VCA) strategies, two representative methodologies have emerged as which constitute the disordered arrangement in LCSON, duration. In addition, lanthanide ions, including even the non-f-significant alloys and solid solutions that consist of similar elements in composite pseudopotential) has been successful for some LCSON. The VCA approximation along with the projector-augmented wave function is not recommended for LCSON. Therefore, a configurational ensemble average approximation based on Boltzmann energy distribution would be a better option for LCSON.

We were particularly interested in calculating a reliable band gap energy for LCSON. The present investigation was motivated by the fact that the highest (maximized) calculated band gap energy was still lower than the experimental value, irrespective of what exchange correlation functionals were used. Such unreliability in the DFT-based band gap calculation originates from the fact that the DFT calculation is inherently concerned with only the ground state. Therefore, DFT systematically underestimates the band gap, particularly for insulators. From a practical point of view, it is customary to pursue a maximized DFT-calculated band gap energy to reach experimental values for inorganic insulator materials. In fact, several dozens of randomly chosen LCSON configurations that involved distinct La/Ca and O/N distributions returned calculation results for total and band gap energies that were more widely scattered than we had expected. Along with a very high variance, we also had a calculated band gap energy that was far below the experimental value. Accordingly, a band gap energy for LCSON that is averaged over randomly chosen configurations would no longer simulate the experimentally measured results.

A reasonable configurational average approach, which is referred to as the site occupancy disorder (SOD) program, has been successfully used for several disordered structures. However, a supercell-based SOD program was expected to be too computationally demanding for an LCSON structure, with a large unit cell size, a large number of atoms in the unit cell, a relatively low symmetry, and a large band gap. The large unit cell size never allows for the construction of an appropriate supercell due to unacceptable computational expenses. Although such a supercell was available, the possible number of configurations (configurational diversity) would be greater and would lead to more scattered band gap energies. The low symmetry was also not very helpful due to a low level of configurational degeneracy. We employed a unit cell model that still had a higher number of atoms in comparison to that in conventional supercells that have been used for typical high-symmetry materials, such as metal alloys and simple high-symmetric inorganic solid solutions. We systematically treated randomly distributed atoms in the LCSON unit cell model. As a result, an extremely large number of possible independent configurations (5184) abide the La$_{4-x}$Ca$_x$Si$_{12}$O$_{30-x}$N$_{18-x}$ (LCSON) stoichiometry, with $x = 1.5$. Obviously, it would be impossible to independently calculate all of these configurations using DFT.

It was apparent that the current state-of-the-art provides no ideal DFT calculation method to tackle the disorder problem for LCSON-like materials with a large number of atoms in a large unit cell, low symmetry, and large band gap. To sort out this problem, however, we employed a pragmatically reasonable strategy, the so-called selected configurational ensemble average method, with the assistance of the elitist nondominated sorting genetic algorithm (NSGA-II) based on the Pareto optimality principle and a small number of more plausible configurations were selected in a systematic manner. Owing to NSGA-II, we could significantly reduce the number of configurations to be considered, and the more computationally demanding calculation methods, such as a hybrid functional calculation, could be applied to only a limited number of configurations; thereby, we accomplished a realistic band gap energy that more closely approximated the experimental measurement.

2. RESULTS AND DISCUSSION

2.1. General Approach for DFT Calculation. The exchange correlation potential used for the preliminary screening via the NSGA-II iteration was based on the generalized gradient approximation (GGA), parameterized by Perdew, Burke, and Ernzerhof (PBE) in the Vienna ab initio simulation package (VASP5.3). The projector-augmented wave (PAW) potentials along with a cutoff energy of 500 eV and a $1 \times 4 \times 2$ k-mesh was adopted using the Monkhorst-Pack scheme. Structural relaxation was implemented for all selected configurations, with the values for atomic position, lattice parameter, and symmetry all allowed to vary. This general relaxation was referred to as a Type I configurational setting. In parallel with the Type I setting, another NSGA-II iteration was independently implemented for atomic position refinement except with fixed lattice parameters and symmetry, wherein the experimentally obtained lattice parameters and C2 symmetry were adopted. This case was referred to as a Type II configurational setting, and the additional NSGA-II result based on the Type II setting is separately presented in the Supporting Information. More details about the Type I and II configurational settings will be discussed in subsection 2.3. After completing the structural relaxation for every configuration, the band structure and density of states (DOS) were also calculated without spin polarization under computation conditions that were the same as those described above, and finally the band gap and total energies were evaluated for use as fitness function values for the NSGA-II iteration.

The GGA-PBE-based NSGA-II result was compared with the experimental data to select appropriate model structures for further computation. The actual optical band gap for LCSON was evaluated as 4.45 eV on the basis of the intersection of a straight line with the energy axis in the $\{F(R)h\}^2$ versus energy ($h\nu$) plot shown in the inset of Figure 1. The absorbance, $F(R)$, was calculated from the diffuse reflectance data using a Kubelka–Munk equation. All of the GGA-PBE-calculated band gap energies were far smaller than the experimental values.
To select configurations for use in further computations, we classified all relaxed configurations that appeared during the NSGA-II iteration. The highest band gaps were 3 and 3.15 eV for Type 1 and II cases, respectively. Further calculations based on more advanced exchange correlation functionals should be employed to tackle the band gap underestimation problems. We adopted only the Type I result for the further calculations. The reason the Type II result was discarded will be explained in detail later in subsection 2.3. We selected seven Type I configurations that exhibited relatively higher band gap energies and lower total energies from all NSGA-II results. These selected configurations are constituents in the first and second Pareto frontiers of all configurations that the NSGA-II iteration produced, which are marked by a red contour in Figure 2.

Thereafter, a hybrid functional involving nonlocal Fock exchange (HSE06)\(^{40-42}\) was adopted for the chosen configurations to obtain a more realistic band gap energy. First, these GGA-PBE-relaxed configurations were used as input model structures and relaxed again in the HSE06 calculation scheme. Subsequently, the DOS and band structures were also obtained in the HSE06 calculation scheme. The final band gap energy was calculated as 4.15–4.46 eV when the HSE06 functional was employed for the relaxed configurations. Although most of them were still slightly lower than the experimental data, a clear improvement was observed in comparison with the GGA-PBE calculation. The HSE06 functional is well known to be highly effective in improving the calculated band gap energy of semiconductors and large-gap insulators.\(^{43}\) In this regard, the hybrid functional (HSE06) calculation remains to be a universal option for oxynitride insulators. A complementary option such as an onsite potential (DFT + U\(^{44-47}\) or HSE + U\(^{48}\)) approach did not give better results in comparison to the HSE06 approach for LCSON. Another option could be meta-GGA calculations, such as a Tran–Blaha modified Becke–Johnson exchange potential approximation,\(^9,30\) which is known to yield band gaps with the accuracy of a hybrid functional. However, that approach did not yield results as good as those that HSE06 gave for the LCSON band gap calculation. The GW approach\(^{45,46}\) was not employed because it is not possible to obtain a quasiparticle band structure for any chosen path through the Brillouin zone by VASP5.3. Consequently, further calculation was implemented totally on the basis of the HSE06 hybrid functional scheme.

It should be noted that we employed a simple GGA-PBE calculation for a large number of configurations of LCSON that appeared during the NSGA-II iteration. Thereafter, a limited number of configurations were chosen out of the NSGA-II iteration results for further calculations using HSE06 to more realistically estimate the approximate band gap energies. Because the GGA-PBE-calculated band gap has a linear relationship with the HSE06-calculated band gap, the high-band-gap configurations selected from the GGA-PBE calculation also led to a high band gap in the HSE06 calculation. In fact, we clearly confirmed a linear relationship between the HSE06- and GGA-PBE-calculated band gaps for LCSON, as shown in Figure 3. Consequently, the chosen configurations proved to be the most superior in terms of GGA-PBE-calculated band gaps for several representative configurations, showing a certain correlation.
calculated as well as the HSE06-calculated band gaps. For a comprehensive understanding of our computation strategy, all procedures are described in detail via the succinct flow chart shown in Figure 4.

![Flow chart elucidating all procedures of the proposed computation strategy.](image)

**Figure 4.** Flow chart elucidating all procedures of the proposed computation strategy.

### 2.2. NSGA-II-Assisted DFT Band Gap Energy Calculation for LCSON

As for the partially occupied structure of LCSON, the La and Ca ions shared the same Wyckoff site in relatively proportional amounts, as shown in the atomic position table along with site occupancy in Table S1. The O and N ions also share several Wyckoff sites. On the basis of the occupancy values for each of the shared Wyckoff sites, which were obtained via Rietveld refinement (Table S1), we reasonably distributed 5 La ions, 3 Ca ions, 33 N ions, and 9 O ions in a unit cell model by obeying the occupancy values of every shared Wyckoff site when constructing the input structure models. Trivial violations in occupancy were allowed for each site, but total occupancy fulfilled the stoichiometry of $\text{La}_{4\times} \times \text{Ca}_{2\times} \times \text{Si}_{1\times} \times \text{O}_{3\times} \times \text{N}_{1\times}$ (LCSON), with $x \approx 1.5$. As a result, the number of plausible configurations was 20,736, which resulted from the following enumerations: $\times \text{C}_1$ (La/Ca1 site) $\times \text{C}_2$ (La/Ca2 site) $\times \text{C}_3$ (N/O1 site) $\times \text{C}_4$ (N/O7 site) $\times \text{C}_5$ (N/O9 site) $\times \text{C}_6$ (N/O11 site). Because there could be many duplications, 20,736 was reduced to 5184 by considering the $C_2$ symmetry, which implies that all of the shared sites are general sites with maximum multiplicity, 4, due to the $C_2$ symmetry. The DFT calculation for four equivalent configurations gave exactly the same total energy and also the same band gap energy. This means that we incorporated all possible independent configurations for the disordered LCSON structure on a unit cell basis by adopting the 5184 models. Note that the 5184 initial models actually violated symmetry principles, which will be discussed in more detail in subsection 2.3.

We took up 5184 input model structures (configurations) for the DFT calculation of LCSON. Although the $C_2$-symmetry-related degeneracy significantly reduced the number of configurations to a quarter of the original total number, it would still be impossible to track down all of these 5184 configurations. We employed a representative metaheuristics strategy to reduce the computation burden and select plausible configurations that would give rise to a more realistic band gap energy as well as a lower total energy. That is, NSGA-II was employed to implement this selection task.26 NSGA-II has been successfully utilized for the discovery of novel phosphors.1−3 Both the total energy and band gap energy were objective (fitness) functions for the present NSGA-II iteration. The decision variable designated each configuration in the entire search space of 5184 different configurations, and each of the Wyckoff sites in Table S1 was parameterized on the basis of whether the sharing element (Ca and O ions) occupied a site of concern; thereby, a vectorized decision variable was used for the NSGA-II iteration. The total energy could be conveniently thought of as being indicative of the stability of a given configuration in place of the enthalpy of formation, as the constituent elements and their molar fractions of LCSON are fixed for all configurations in the decision variable space. Thus, the total energy was minimized in the NSGA-II process. In parallel with the total energy, the difference in the band gap energy between the calculated and experimentally measured results was taken as an objective function to be minimized. This implies that we minimized the total energy and at the same time maximized the band gap energy during the NSGA-II iteration. The population size was 16, a tournament selection was adopted, and the crossover and mutation rates were 80 and 30%, respectively. NSGA-II differs from a conventional NSGA in that two consecutive generations are merged to generate the next, which indicates a so-called elitism-reinforced NSGA-II. Owing to this treatment, NSGA-II converges much faster than the conventional NSGA.26 A more detailed description is available in our previous reports.1,2

Figure 5 shows a plot of band gap energy versus total energy (two fitness functions) for all generations from the first to the tenth. Each generation consisted of 16 configurations. The first generation that was chosen stochastically was a prominent diversity in the calculated band gap energy (0.23−2.53 eV) and total energy ($\approx$593.991 to $\approx$590.368 eV). The evidence that evolution took place was conspicuously observed, that is, the population converged and many identical entries appeared as it progressed to later generations. The arrow in Figure 5 indicates the evolution direction, namely, minimizing the total energy and maximizing the band gap energy. Figure 6 shows the relaxed configurations of the first and last generations viewed in the $b$ direction, along with the total DOS and calculated band gap energies. Structural relaxation based on the GGA-PBE functional did not significantly change the LSCON structure and only allowed small changes: <0.01 Å in lattice size and
<0.5° in lattice angle. Although it was difficult to note an evolutionary trend in terms of the configurational change, it was easy to detect reduced diversity such that the number of identical configurations increased as the NSGA-II iteration progressed to later generations. The duplication was due to a small search space that included only 5184 entries. Although this search space size was huge when considering that in the DFT calculation, it was relatively small in view of a conventional NSGA-II optimization task. The mean and variance values and the covariance for both the fitness function values (the total and band gap energies) in the randomly chosen first generation could be approximated to the true mean and covariance values for all configurations, as we also obtained similar mean and covariance values for another random sample consisting of 24 configurations. This means that a very low mean value for a band gap energy with great diversity could be anticipated for all 5184 configurations. However, the values for the mean and covariance of later generations were dramatically increased and decreased, respectively. As far as the band gap energy was concerned, the configurational average for the entire configuration ensemble did not match well with the actual experimental value. Instead, selected configurations out of later generations would be better to obtain a more realistic averaged band gap energy.

The 10th generation exhibited a remarkable improvement in both the total and band gap energies, with a reduced covariance. Therefore, we confirmed the enhanced band gap energy and reduced total energy in comparison with those of the randomly chosen first generation. The arrow in Figure 5 marks the dramatic evolution. Pareto optimality (or Pareto sorting) is a key idea constituting NSGA-II, which drove the Pareto front to move in the optimization direction as it minimized the total energy and simultaneously maximized the band gap energy, while either niche expansion or maximization of the crowding distance was pursued. In fact, NSGA-II exerts a better effect when the fitness (objective) functions trade off of each other, but in our case, the total energy was parallel with the band gap energy. It is certain that there is a strong inverse correlation between the total and band gap energies, that is, the

Figure 5. All populations from the first to the tenth generation; the arrow indicates the evolution direction.
higher the band gap the lower the total energy, with no trade-off. In this regard, Figure S clearly shows that a conspicuous optimization (evolution) took place in a left-upward direction, as indicated by the arrow, according to the Pareto optimality principle. We stopped the NSGA-II iteration at the 10th generation. Ten generations were sufficient to obtain an acceptable convergence because the NSGA-II iteration was run in such a small, discrete decision variable space (=search space) using only 5184 candidates. The maximum band gap energy calculated on the basis of DFT–GGA appeared at the sixth generation, and no higher value appeared afterwards.

We gathered all of the configurations that appeared during the NSGA-II iteration from the first to tenth generation and Pareto-sorted them, as shown in Figure 2. It should be noted that the Pareto sorting shown in Figure 2 was carried out until the 7th Pareto frontier, with no distinction between generations. Particular attention was drawn to configurations with higher band gap energies obtained from the NSGA-II iteration. In this regard, we pinpointed an optimized sample consisting of the first and second Pareto frontiers, as marked by the red contour in Figure 2, which had a higher band gap energy and lower total energy. The seven different configurations in this selected sample were used in averaging the band gap energy. These configurations used in averaging the band gap energy constituted a so-called selected configurational ensemble. We were not interested in an average under the GGA calculation scheme because the maximum band gap energy value (3 eV) in this ensemble remained far below the actual value (4.45 eV). The GGA-based DFT calculation gave a band gap energy that was lower than the actual value for almost all insulators. To improve the band gap energy calculation, a further DFT calculation scheme was employed.

We executed a hybrid functional calculation (HSE06) involving a fraction of the exact exchange (Hartree–Fock exchange) potential for the configurations taken out of the first and second Pareto frontiers in Figure 2. These configurations were relaxed in the GGA-PBE calculation scheme and exhibited a relatively higher level of GGA-PBE band gap energy. On the basis of a version of the Boltzmann energy distribution that ignores the vibrational and pressure effects of thermodynamics, as previously established by Grau-Crespo et al.,

\[
E_{\text{g}}^{\text{Av}} = \frac{1}{Z} \sum_{i=1}^{7} e^{-E_{\text{g}}^{(i)}/k_{\text{B}}T}, \quad Z = \sum_{i=1}^{7} e^{-E_{\text{g}}^{(i)}/k_{\text{B}}T} \tag{1}
\]

where \(E_{\text{g}}^{(i)}\) is the HES06-calculated band gap, \(E_{\text{g}}^{(i)}\) is the HES06-calculated band gap, \(E_{\text{g}}^{(i)}\) is the energy of the \(i\)th configuration in the selected sample, and \(k_{\text{B}}\) is the Boltzmann constant. As a result, we could more closely approximate the experimentally measured band gap energy. The average band gap (\(E_{\text{g}}^{\text{Av}}\)) for this selected group was 4.26 eV at room temperature. Such an average incorporates the probability density distribution based on the appearance frequency in a systematic manner. However, in the case of LCSON, the appearance frequency of each configuration was assumed to be uniform; thus, the average based on Boltzmann energy distribution should not significantly differ from the simple arithmetic mean. The configurational uniformity was judged on the basis of use of the unrelaxed configuration as an input model for the NSGA-II iteration, rather than on the use of the relaxed configuration after DFT calculation. In fact, none of the relaxed configurations should be the same from a strict point of view.

It should be noted that only a small number of configurations selected by NSGA-II were used to make a reliable estimation of the band gap energy of LCSON, and their representativenesses would be acceptable. The Boltzmann energy distribution-based average over the entire population would have given a much lower band gap, which would have deteriorated the representation. Moreover, it was practically impossible to involve a large number of configurations to evaluate the average because the use of the HSE06 functional would have given rise to considerable computational demands. It should be noted that such an enhanced band gap energy (4.26 eV) almost reached the actual value (4.45 eV). Owing to this pragmatic method of simulating the band gap energy, it was possible to more closely approximate the experimental band gap energy for such a disordered inorganic compound with such a large unit cell made up of many atoms, a low symmetry, and a large band gap. If we had restricted the number of configurations, for instance, if only the first Pareto frontier in Figure 2 had been adopted, then a more reasonable band gap energy would have been obtained.

As a matter of fact, calculation of the band structure and DOS for a specific configuration would make no sense from a strictly theoretical point of view. However, Figure 7 shows a

![Figure 7. Band structure along with DOS for an LCSON configuration (upper figure) that gave the highest band gap energy in the HSE06 calculation.](image)
selected configurational ensemble and must be regarded as neither an optimized nor an ideal structure for LCSON.

2.3. Limitations of the Configuration Setting in Deciding the True Structural Model. Once we chose either the configurational ensemble average approximation or the VCA approach for the DFT calculation, we had a pragmatic approximation rather than an exact theoretical approach. Thus, it was meaningless to wrestle with crystallographic details and small violations of the core principles of crystallography. For instance, there was no way to set up a perfectly reasonable configuration set for the configurational ensemble average approximation. For the sake of convenience, we adopted two different configurational setups, as described in the preceding subsection: Type I and Type II.

The Type II setting did not allow for a lattice parameter change, and only the atomic positions were allowed to vary during the structural relaxation. This meant that the atomic arrangement certainly violated the $C_2$ symmetry, even when the lattice parameters were preserved as those of a monoclinic parent structure. It is obvious that the Type II model slightly violated the crystallographic symmetry principle. This meant that the specific Ca/La and O/N configurations removed both the twofold rotation and the C-centered translation symmetries but maintained the monoclinic structural frame, which implies that the optimum relaxed configuration should be neither a $C_2$ nor a $P1$ symmetry but rather a nonexistent symmetry. Surprisingly, however, the VASP5.3 allows such a slight violation. Thus, we completed the NSGA-II iteration using a Type II configurational setting and obtained a very similar result for the Type I setting, wherein the crystallographic principle was not violated. All Type II calculated results corresponding to Figures 2, 5, and 6 for Type I are given in Figures S2 and S3.

In principle, it would be possible to constitute a $P1$ symmetry by allowing variation in the lattice parameters during the structural relaxation, which refers to the Type I configurational setting. In fact, we adopted a lattice parameter relaxation for all configurations during the entire NSGA-II process. As a result, the lattice experienced very little distortion during the relaxation, but such a small change definitely constituted $P1$ symmetry. Despite such completeness that violated no principle, a minor complication arose when the Type I setting was adopted. Virtual XRD patterns simulated on the basis of the Type I relaxed structures deviated slightly from the actual XRD pattern of LSCON, whereas the simulated XRD pattern obtained from the Type II setting more closely resembled the experimental XRD pattern, despite the trivial appearance of additional superlattice peaks. However, it should be noted that the virtual XRD simulation based on a unit cell configuration model must not represent the actual structure at all. Consequently, the Type I setting was considered more significant in the present investigation, as it violated no principle of crystallography. Thus, the results from only the Type I setting are displayed in the main text of the present article, and the results of the Type II settings are presented in the Supporting Information. As far as the calculated band gap was concerned, however, both the Type I and II settings yielded similar results.

With powder XRD- and neutron diffraction-based refinements, such an averaged (smeared, partially occupied, or disordered) structure should be tangible via the composite atomic scattering factor. This appears to be analogous to the VCA approach involving the composite pseudopotential. On the other hand, every single configuration belonging to a configurational ensemble would accept an accurately defined, and unique, atomic arrangement. Rietveld refinement based on either XRD or neutron diffraction data can provide nothing but mathematically adjusted structural information, and the actual structure would be incomprehensible for disordered materials with a large cell, low symmetry, and large band gap. The disorder should not be restricted to a unit cell scale but should instead be extended to a greater scale that covers a number of cells. Such a situation cannot be simulated by adopting a single unit cell model, irrespective of the use of either a configurational ensemble average approximation or a VCA approximation. However, a supercell approach, which would be only the option, was also impossible for a large cell with a large number of atoms.

It should be noted that the configuration with a calculated band gap energy that best matched the experimental value was a virtual structure that will never be realized via an actual experiment. In this regard, it is not recommended to argue that this structure is optimum and scientifically meaningful. Nonetheless, it is worthwhile to average those well-matched configurations that differ from one another. In this regard, we suggest a pragmatic strategy to calculate the realistic band gap energy through DFT calculation for disordered structures with a large cell, low symmetry, and large band gap, which we are frequently faced with in inorganic functional materials groups. Given the current state-of-the-art, no existing strategy can exactly simulate the band gap energy of such a disordered structure.

3. CONCLUSIONS

In conclusion, we proposed a pragmatic DFT calculation scheme that will enable an acceptable band gap energy calculation for disordered structures with a large unit cell size, relatively low symmetry, and large band gap. Using the proposed strategy, we successfully calculated an acceptable band gap energy for a representative disordered LCSON structure. This strategy involved NSGA-II iterations within a 5184-member systematically chosen configuration pool and finally pinpointed several plausible configurations and allowed them to be averaged on the basis of the Boltzmann energy distribution. The NSGA-II process, which is a preliminary screening of a large number of configurations, was executed on the basis of a fast, but inaccurate, GGA-PBE calculation, and the final configurational average was obtained using a more accurate, albeit more time consuming, HSE06 calculation, which drove the calculated results closer to the experimental values. As a result, we calculated the band gap energy of LCSON to be 4.26 eV, which closely approximated the experimental value (4.45 eV).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00190.

Luminescent property of LCSON, detailed crystallographic data of LCSON, and all Type II calculated results (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: kssohn@sejong.ac.kr.
Author Contributions

$^8$W.B.P. and S.U.H. contributed equally. The article was written through contributions of all authors. All authors have given approval to the final version of the article.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the Creative Materials Discovery Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT, and Future Planning (2015M3D1A1069705). A special thanks to Prof. K. Sohn, Choongang University, for his advice regarding the metaheuristics computation.

ABBREVIATIONS

LCSON, La$_{x}$-Ca$_{x}$Si$_{12}$O$_{32}$N$_{18}$; NSGA-II, elitist nondominated sorting genetic algorithm; DFT, density functional theory; GGA, generalized gradient approximation; PBE, Perdew, Burke, and Ernzerhof; HSE, Heyd, Scuseria, and Ernzerhof; DOS, density of states; PAW, projector-augmented wave; SOD, site occupancy disorder

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