Toward the Rational Design of Mid-Infrared Nonlinear Optical Materials with Targeted Properties via a Multi-Level Data-Driven Approach

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Design and exploratory synthesis of new mid-infrared (mid-IR) nonlinear optical (NLO) materials are urgently needed for modern laser science and technology because the widely used IR NLO crystals still suffer from their inextricable drawbacks. Herein, a multi-level data-driven approach to realize fast and efficient structure prediction for the exploration of promising mid-IR NLO materials is proposed. Techniques based on machine learning, crystal structure prediction, high-throughput calculation and screening, database building, and experimental verification are tightly combined for creating pathways from chemical compositions, crystal structures to rational synthesis. Through this data-driven approach, not only are all known structures successfully predicted but also five thermodynamically stable and 50 metastable new selenides in $A^{I}B^{III}$ Se₂ systems (A^{I} = Li, Na, K, Rb, and Cs; B^{III} = Al and Ga) are found, among which eight outstanding compounds with wide bandgaps (> 2.70 eV) and large SHG responses (>10 pm V^{-1}) are suggested. Moreover, the predicted compounds 142d-LiGaSe2 and 14/mcm-KAlSe2 are successfully obtained experimentally. In particular, LiGaSe₂ exhibits a robust SHG response ($\approx 2 \times AGS$) and long IR absorption edge that can cover two atmospheric windows (3-5, 8-12 µm). Simultaneously, this new research paradigm is also applicative for discovering new materials in other fields.

1. Introduction

Nonlinear optical (NLO) materials are of great importance in the application of medical treatment, laser communication, and laser lithography via laser frequency conversion.^[1–7] In the past decades, numerous NLO materials such as β -BaB₂O₄ (BBO),^[8]

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LiB₃O₅ (LBO),^[9] KTiOPO₄ (KTP),^[10] and KBe₂BO₃F₂ (KBBF)^[11] have been explored or/and widely applied in the ultraviolet (UV) and visible spectral regions.^[12,13] By contrast, only a few NLO materials are commercially available in the mid/far-IR region $(2.0-20 \,\mu\text{m})$ to date, such as AgGaQ₂ (Q = S, Se)^[14,15] and ZnGeP₂.^[16] Unfortunately, they have some inherent drawbacks including low laser damage threshold (LDT) or severe two-photon absorption at 1 µm, which greatly limits their practical applications. Therefore, the development of novel IR NLO materials with high performances is urgently demanded.^[17,18] However, a potential mid-IR NLO material should satisfy the strict criterion: a wide bandgap to ensure large LDT, good IR transparency to cover atmospheric windows (3-5 µm, 8-12 µm), strong second harmonic generation (SHG) coefficient ($|d_{ii}| > 1/2$ AGS, AGS has a SHG coefficient about 13.4 pm V⁻¹). Since the contradiction between the bandgap and SHG coefficient renders the difficulty in balancing the NLO performances in one

compound, how to explore new NLO materials with balanced properties becomes one of the key research issues.

Owing to the extremely rich structure types and amazing performances, chalcogenide has become one preferred system to explore mid-IR NLO materials.^[19-21] Accordingly, a batch of chalcogenides such as $LiMQ_2$ (M = Ga, In, Q = S, Se),^[22–24] BaM_4Q_7 (M = Al, Ga, Q = S, Se), ^[25–28] Li₂In₂MQ₆ (M = Si, Ge; Q = S, Se),^[29] BaGa₂MQ₆ (M = Si, Ge; Q = S, Se),^[30] AXHg₃P₂S₈ (A = Rb, Cs; X = Cl, Br)^[31] AgLiGa₂Se₄^[32] Na₂ZnGe₂S₆^[33] CuZnPS₄,^[34] and CuCd₃PS₆^[35] have been reported and exhibited good NLO properties in some specific aspects such as bandgap and/or SHG response. This stimulates us to continue to search for promising sulfides/selenides for mid-IR NLO applications. Compared with sulfides, selenides generally perform longer IR absorption edge and stronger SHG response, but narrower bandgap that will result in low LDT that is not conducive to high power laser output. Therefore, it is still a big challenge to design novel selenides with balanced performance (large SHG response and high LDT).

With the rapid development of high-performance computing, computer-aided materials design system has become

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an effective way to explore new materials with targeted properties.^[36–39] At present, there are generally two main computational approaches for functional material exploration: 1) to screen known materials with excellent properties in material databases (e.g., ICSD) using high-throughput (HT) computation and screening techniques^[40,41]; and 2) to predict hitherto unknown materials with the help of crystal structure prediction algorithms.^[42–46] Although giant success has been achieved through them in discovering excellent candidate materials, there are still huge challenges in multi-level screening and efficient prediction.

In this work, we proposed a multi-level data-driven approach to realize fast and efficient structure prediction for the exploration of promising mid-IR NLO materials. First, ten chemical compositions of $A^{I}B^{III}$ Se₂ (A^{I} = Li, Na, K, Rb, Cs; B^{III} = Al, Ga) with wider bandgaps than 2.50 eV stand out from 325 chemical systems by machine learning method (Atom Table Convolutional Neural Networks-ATCNN).^[47] Subsequently, structure analogy technique and global structure search were executed for them, 64 compounds within thermodynamically synthesized region were discovered, their computed formation enthalpies above thermodynamical convex hull (E_{hull}) are less than 0.1 eV atom⁻¹. Simultaneously, their bandgaps and optical properties were also evaluated; for bandgap, there are 42 compounds with the bandgap larger than 2.70 eV; 15 compounds with expected bandgap (>2.70 eV) crystallize in non-centrosymmetric space groups, 11 of them show large SHG response exceeding 1/2 AGS. Moreover, eight compounds can satisfy the strict condition for the figure of merits and realize the balance of wide bandgap and large SHG response ($E_{g} > 2.70$ eV, $|d_{ij}| > 10 \text{ pm V}^{-1}$). One of the significant breakthroughs is that the predicted structures (I42d-LiGaSe₂ and I4/mcm-KAlSe₂) were obtained experimentally, which directly proves the feasibility of our proposed method. And I42d-LiGaSe₂ shows obvious advantages in SHG response (≈2 × AGS) and IR absorption edge (>12 μ m). This work makes a thorough prediction of $A^{I}B^{III}$ Se₂ (A^{I} = Li, Na, K, Rb, Cs; B^{III} = Al, Ga) for the first time, we believe that the forward-looking studies will inspire researchers to explore novel mid-IR NLO materials in the field of ternary selenides.

2. Computer-Aided Design Blueprint

Figure 1 shows our well-designed target-driven materials discovery workflow for exploring promising mid-IR NLO materials. It mainly contains the following three parts:

The first part is the fast determination of potential chemical systems with wide bandgaps because the chemical space of selenides is very huge, exploring them one by one in known databases is unrealistic. To achieve this goal, we used the state-of-art machine learning method ATCNN^[47] for rapidly predicting E_{σ} of materials in which the chemical composition is the only input. We tested this method for those available selenides or sulfides and found that the predicted bandgaps agree well with those reported values (see Table S1, Supporting Information). Using this method, we predicted E_{α} for 3887 ternary selenides in $c_{26}^2 = 325$ A-B-Se systems (A and B are two different elements chosen from Li, Na, K, Rb, Cs, Cu, Ag, Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Sn, Pb, B, Al, Ga, In, Tl, Sc, Y, Si, and Ge), as uploaded in our Novel Opto-Electronic Materials Database (NOEMD).^[48] Among the whole studied selenides, 1620 ternary selenides have the predicted E_{α} values larger than 2.5 eV, indicating the effectiveness and necessity of our proposed method for the determination of potential chemical systems to explore promising mid-IR NLO selenides.

The second part is crystal structure prediction. For a given chemical composition with expected $E_{\rm g}$, we then evaluated its thermodynamical possibility for exploratory synthesis. First, using the chemical composition as input, the advanced structure analogy technique was employed to quickly construct crystal structures in this chemical composition.^[49,50] We noted that, for a given chemical composition, structure analogy techniques can quickly predict several low-energy structures, although the structure with global minimum energy may be missed. For all structures generated by structure analogy technique, we performed fully structure relaxation and total energy calculation and computed their E_{hull} . Herein, we used $E_{\text{hull}} = 0.1 \text{ eV}$ atom⁻¹ as a guiding principle to distinguish structures with good thermodynamical stability.^[51] For those structures with $E_{\rm hull}$ less than 0.1 eV atom⁻¹, we considered them as stable $(E_{\text{hull}} = 0 \text{ eV atom}^{-1})$ or metastable (0 eV atom $^{-1} < E_{\text{hull}} \le 0.1 \text{ eV atom}^{-1}$) structures, whereas other structures with E_{hull} larger than 0.1 eV atom⁻¹ were regarded as unstable structures.



Figure 1. The well-designed target-driven materials discovery workflow used for exploring novel promising mid-IR NLO materials.

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For those chemical compositions containing thermodynamically stable/metastable structures generated by structure analogy technique, we considered them as potential thermodynamically stable chemical compositions and then further performed evolutionary global search algorithm to confirm their lowest energy structures because the evolutionary algorithm has advantages over structure analogy technique on discovering the global minimum energy structure. When a new lowest energy structure is predicted by the evolutionary algorithm, E_{hull} will be recalculated and updated for all structures in this composition to make sure that the lowest energy compound is found.

The third part is HT properties calculation, for all thermodynamically stable/metastable structures generated by structure analogy technique and evolutionary crystal structure research, we first performed HT band gap computation based on HSE06 functional and then screened structures with bandgap values greater than 2.70 eV (the screening benchmark). For those structures with targeted bandgaps, we then performed HT optical properties calculation (SHG coefficient tensors $|d_{ij}|$, birefringence Δn). After that, we can screen potential mid-IR NLO materials according to the screening criteria ($E_{g} > 2.70$ eV and $|d_{ij}| > 10 \text{ pm V}^{-1}$). Herein, we noted that the screening criteria $(E_{\alpha} > 6.20 \text{ eV and } |d_{ii}| > 0.39 \text{ pm V}^{-1})$ can be set for the discovery of deep-UV NLO materials. After the candidate structures were screened out, they will be saved in our materials databases that in turn provide guidance for future new material discovery. For those promising mid-IR selenides, they can be verified experimentally.

3. Results and Discussion

3.1. Potential Chemical Compositions to Crystal Structures

We used ATCNN method to dig out potential advantageous chemical compositions ($E_g > 2.50$ eV) for exploring mid-IR NLO materials. First, 325 chemical systems can be attained from

A-B-Se systems (A and B are two different elements chosen from Li, Na, K, Rb, Cs, Cu, Ag, Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Sn, Pb, B, Al, Ga, In, Tl, Sc, Y, Si, and Ge). We then sampled 3887 ternary selenides with the chemical formula $A_x B_y \text{Se}_z$ (*x*, *y*, *z* \leq 8, the chosen compositions have been considered the charge neutrality and electronegativity balance tests). According to Figure 2a, it can be found that the chemical systems containing alkali metal (Li, Na, K, Rb, Cs) and alkaline earth metal (Mg, Ca, Sr, Ba) cations are beneficial to generating large bandgap. Based on this recommendation, we herein focused on chemical systems in which the A-site is an alkali metal to explore mid-IR NLO materials with large bandgap. For the B-site, we selected Al or Ga; on the one hand, they can generate relative large bandgap, on the other hand, in those known Al- or Ga-contained selenides, they generally form [AlSe4] or [GaSe4] units which were suggested to be beneficial to SHG coefficient.^[25-29] And the rest of chemical systems are suggested for further studies. For the studied A-B-Se system (A = Li, Na, K, Rb, Cs; B = Al, Ga), stoichiometric ratios mainly include 4:2:5, 5:3:7, 7:1:5, 8:2:7, 7:3:8, 3:1:3, 5:1:4, 1:1:2, 1:3:5, 2:4:7, and 1:5:8. As shown in Figure 2b, 1:1:2 shows comparable advantage in bandgap compared with the others. Finally, ten chemical compositions of $A^{I}B^{III}$ Se₂ (A^{I} = Li, Na, K, Rb, Cs; $B^{\text{III}} = \text{Al}$, Ga) were used preferentially for next research.

We used the structure analogy technique to generate structures for each composition of $A^{1}B^{111}$ Se₂ (A^{I} = Li, Na, K, Rb, Cs; B^{III} = Al, Ga) and preformed fully structure relaxation and total energy calculation for all generated structures. By combining with materials project (MP) database, we then calculated E_{hull} for the whole structures generated by structure analogy technique. We found that all these ten compositions contain potential thermodynamically stable structures (see Table S2, Supporting Information).

We further performed evolutionary structure search for all these ten compositions to confirm their lowest energy structures. We found that the lowest energy structures were updated in NaGaSe₂, RbAlSe₂, CsAlSe₂, and CsGaSe₂ (see Table S3, Supporting Information). Herein, we noted that, among the lowest energy structures predicted for each composition, four



Figure 2. a) Distribution of bandgaps of 3887 samples based on A-site cation; b) The heat map of stoichiometric ratios of A-B-Se systems (A = Li, Na, K, Rb, Cs; B = Al, Ga).

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structures (C2/*c*-KAlSe₂, C2/*c*-KGaSe₂, C2/*c*-RbGaSe₂, and C2/*c*-CsGaSe₂) have been reported by MP/ICSD, while the other six are still not included in any known material databases.

Experimentally, several compounds in $A^{I}B^{III}Se_{2}$ ($A^{I} = Li$, Na, K, Rb, Cs; $B^{III} = Al$, Ga) system were synthesized (see Table S4, Supporting Information). Comparing Tables S3 and S4 (Supporting Information), it is found that five compounds (I42d-LiGaSe2, C2/c-KAlSe2, C2/c-KGaSe2, C2/c-RbGaSe2 and C2/c-CsGaSe₂) of the predicted thermodynamically stable compounds in $A^{I}B^{III}Se_{2}$ (A^{I} = Li, Na, K, Rb, Cs; B^{III} = Al, Ga) system have been synthesized experimentally, the predicted cell parameters are consistent with corresponding experimental parameters, indicating feasibility of our proposed method in exploration new materials. And it is worth to note that thermodynamically metastable materials can also exist and are ubiquitous in nature.^[52] A typical case is diamond versus graphite; the energy of diamond is higher than that of graphite at ambient conditions, but diamond can also exist. In this work, we also found that the calculated E_{hull} of $Pna2_1$ -LiGaSe₂, C2/c-NaAlSe₂, I4/mcm-NaAlSe₂ are 0.002, 0.009, and 0.028 eV atom⁻¹, respectively, whereas they were synthesized experimentally. Therefore, this thermodynamically stable/ metastable selenides are considered for the next structure description and properties investigation.

3.2. Crystal Structure Characterization

For $A^{1}B^{III}$ Se₂ (A^{I} = Li, Na, K, Rb, Cs; B^{III} = Al, Ga) system, the space group, atom number, volume, total energy, E_{hull} , bandgap, birefringence, and $|d_{ij}|$ of compounds fall within the defined "metastable window" of 0.1 eV atom⁻¹ are listed in Table S5 (Supporting Information). Herein, we take LiGaSe₂ as an example to describe their crystal structure. **Figure 3** exhibits crystal structures and the corresponding E_{hull} of each phase of LiGaSe₂ generated crystal structure prediction, the others are in Figure S1 (Supporting Information). $I\overline{4}2d$ -LiGaSe₂: tetragonal LiGaSe₂ crystal is the CuFeS₂-type structure, which can be considered as a ternary superstructure of the zinc blende structure. Each Li and Ga atom coordinates with four Se atoms to form asymmetric [LiSe₄] and [GaSe₄] tetrahedral configuration, respectively; [LiSe₄] and [GaSe₄] tetrahedra are interconnected to form tetrahedral stacking layers, which are arranged in an AABB sequence to constitute a 3D network structure.

*Pna2*₁-LiGaSe₂: the orthorhombic LiGaSe₂ crystal is the β -NaFeO₂-type structure, presenting a distorted superstructure of the wurtzite structure; the double [LiSe₄] and double [GaSe₄] tetrahedra are alternately arranged to form two types of layers (layers A and B), which are further stacked in an ABAB sequence to build final structure.

 $Pmc2_1$ -LiGaSe₂: the structure of $Pmc2_1$ -LiGaSe₂ is similar to that of orthorhombic phase ($Pna2_1$ -LiGaSe₂), the difference is that single [GaSe₄] and single [LiSe₄] are connected with each other to construct AA stacking layers in $Pmc2_1$ -LiGaSe₂.

 $P4_12_12$ -LiGaSe₂: [LiSe₄] and [GaSe₄] tetrahedra are alternately connected to form two types of six-membered rings which are further arranged along the *c* direction by sharing Se atoms.

 $P2_1/c$ -LiGaSe₂: [LiSe₄] and [GaSe₄] tetrahedra are arranged with each other to form same six-membered rings, and these six-membered rings are interconnected by sharing Se atoms to form 3D structure.

3.3. Bandgap and Optical Properties Calculation and Screening

The bandgap is one of the most important properties for materials, and it generally can be used to estimate the magnitude of LDT of a compound. We analyzed the bandgap distribution (**Figure 4**a) for stable and metastable compounds calculated by using the HSE06 functional. It can be found that the bandgaps of $A^{I}AISe_{2}$ ($A^{I} = Li$, Na, K, Rb, Cs) are generally greater than 2.70 eV, with the maximum value up to 3.93 eV. Compared with Al-based ternary selenides, $A^{I}GaSe_{2}$ ($A^{I} = Li$, Na, K, Rb,



Figure 3. Crystal structures and the corresponding E_{hull} of each phase of LiGaSe₂.





Figure 4. a) Bandgaps obtained by the HSE06 functional of $A^{I}B^{III}$ Se₂ system ($A^{I} = Li$, Na, K, Rb, Cs; $B^{III} = AI$, Ga) with $E_{hull} < 0.1 \text{ eV}$ atom⁻¹; and b) maximum SHG coefficient distribution for the 15 non-centrosymmetric compounds with the bandgap > 2.70 eV in the $A^{I}B^{III}$ Se₂ system ($A^{I} = Li$, Na, K, Rb, Cs; $B^{III} = AI$, Ga).

Cs) compounds have relatively smaller bandgaps, mostly within the range of 2.0–3.0 eV. Aiming at the bandgap larger than the screening benchmark 2.70 eV, there are 42 compounds, namely, 31 compounds in A^{I} AlSe₂ and 11 compounds in A^{I} GaSe₂ (A^{I} = Li, Na, K, Rb, Cs).

For NLO materials, crystallization in non-centrosymmetric space groups is the precondition. Within 42 compounds, there are a total of 15 non-centrosymmetric compounds, of which 13 compounds are from the A^{1} AlSe₂ system and two from the A^{1} GaSe₂ system. Furthermore, their SHG coefficients were calculated based on sum-over-states approximation. Figure 4b shows SHG coefficient distribution expanding from 5.00 to 23.93 pm V⁻¹ for the 15 non-centrosymmetric compounds with the band gap > 2.70 eV. There are six A^{1} AlSe₂ and two A^{1} GaSe₂ (A = Li, Na, K, Rb, Cs) compounds that can realize the balance between wide bandgap (>2.70 eV) and large SHG coefficient (>10 pm V⁻¹), which are $Pna2_1$ -LiGaSe₂, $I\overline{4}2d$ -LiGaSe₂, $I\overline{4}2d$ -RbAlSe₂, and $I\overline{4}2d$ -CsAlSe₂, respectively.

3.4. Highlighted Materials with Good NLO Performances

The challenge of exploring mid-IR NLO materials is to achieve the balance between bandgap and SHG response. When the figure of merits (bandgap and SHG response) are considered comprehensively, eight compounds (Pna21-LiGaSe2, I42d-LiGaSe₂, Fdd2-KAlSe₂, $Pna2_1$ -KAlSe₂, $I\overline{4}2d$ -KAlSe₂, Pna21-RbAlSe2, I42d-RbAlSe2, and I42d-CsAlSe2) with $E_{\rm g}$ > 2.70 eV and $|d_{\rm ij}|$ > 10 pm V⁻¹ were screened out. For Pna21-LiGaSe2, its optical properties were explored experimentally.^[24,53–55] Concerning $I\overline{4}2d$ -LiGaSe₂, only the chalcopyrite structure type of powder-resolved LiGaSe₂ was reported in 2010,^[56] but single crystal diffraction data and properties characterizations have not been reported so far. With respect to Fdd2-KAlSe2, Pna21-KAlSe2, I42d-KAlSe2, Pna21-RbAlSe2, I42d-RbAlSe2, and I42d-CsAlSe2, they have not been synthesized experimentally to date, we further performed dynamic stability analysis for them. As shown in Figure S2 (Supporting Information), no imaginary frequencies were observed for Pna21-KAlSe2, I42d-KAlSe2, Pna21-RbAlSe2, I42d-RbAlSe2, and I42d-CsAlSe₂, indicating their dynamical stability.

3.5. Experimental Verification

The synthesis of the predicted compounds was tried, and two compounds of I42d-LiGaSe2 and I4/mcm-KAlSe2 were synthesized successfully. The chalcopyrite LiGaSe2 was synthesized via a high-temperature solid-state method with the excess of Se as the flux (experimental details are given in the Supporting Information). Single-crystal XRD analysis indicates that LiGaSe₂ crystallizes in $I\overline{4}2d$ space group with a = 5.843 (2) Å, c = 10.614 (8) Å, Z = 2. The predicted lattice parameters of $I\overline{4}2d$ -LiGaSe₂ are a = 5.925 Å, c = 11.015 Å, Z = 4, the error range is within 2%, which proves the rationality of our predicted structure. The crystal data, structure refinement, atom coordinates, isotropic displacement parameters, and the calculated results of bond valence sum (BVS) for I42d-LiGaSe2 verify the reasonability of crystal structure (Tables S6 and S7, Supporting Information). The crystal structure of the synthesized LiGaSe₂ is shown in Figures 5a,b, and is consistent with the predicted structure described above.



Figure 5. a) ∞ [LiSe₃] and ∞ [GaSe₃] zig-zag chains in $\overline{I42d}$ -LiGaSe₂; b) Chalcopyrite structure of $\overline{I42d}$ -LiGaSe₂; c) A layer with [KSe₈] rings and [AlSe₄] tetrahedra; d) The 3D structure of $\overline{I4/mcm}$ -KAlSe₂.

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I4/mcm-KAlSe2 was also successfully synthesized through the high-temperature solid-state method. Single-crystal XRD suggests that KAlSe₂ crystallizes in the tetragonal space group I4/mcm with a = 8.2246 (4) Å, c = 6.0572 (4) Å, Z = 4 (Table S6, Supporting Information), which are in good agreement with the predicted cell parameters (a = 8.2129 Å, c = 6.5057, Z = 4). The rationality of crystal structure of KAlSe₂ is also verified by the structure refinement, calculated bond valences, atom coordinates, and the equivalent isotropic displacement parameters (Tables S6 and S7, Supporting Information). The asymmetric unit in KAlSe₂ contains one crystallographically independent K atom, one Al atom, and one Se atom. In the structure of KAlSe2, four [KSe8] polyhedra are connected to each other to form a four-membered-ring motif by sharing edges, and the [AlSe4] tetrahedra locate within the 4-MR motifs to build layers (Figure 5c), which are further stacked along the *c* direction to form the 3D structure (Figure 5d). The structure of KAlSe₂ is the same as predicted structure of I4/mcm-KAlSe₂.

The phase purity of $I\overline{4}2d$ -LiGaSe₂ is also confirmed by the PXRD measurement (**Figure 6**a), and it is shown that experimental pattern matches well with the simulated one derived from CIF data which further demonstrates the accuracy of the structural models for $I\overline{4}2d$ -LiGaSe₂. The powder SHG responses were estimated using the Kurtz and Perry method under laser radiation with a wavelength of 2090 nm, and AGS was taken as the reference. As shown in Figure 6b, the SHG intensities of $I\overline{4}2d$ -LiGaSe₂ increase with increase in the particle size, indicating that it is a type I phase-matching NLO material, which is very significant for practical applications. Moreover, the SHG response of $I\overline{4}2d$ -LiGaSe₂ is two times than that of commercial AGS powder at the particle size of 180–212 µm, which is larger than typical chalcogenide IR NLO

crystals, e.g., LiInSe₂ ($\approx 0.9 \times AGS$),^[53] BaAl₄S₇ ($\approx 0.5 \times AGS$),^[25] BaGa₄S₇ ($\approx 1 \times AGS$),^[27] Pna2₁-LiGaSe₂ ($\approx 1.4 \times AGS$).^[54]

The UV-Vis-NIR diffuse reflectance spectrum (Figure S3. Supporting Information) shows that $I\overline{4}2d$ -LiGaSe₂ is a semiconductor with an optical bandgap of 1.71 eV. Although the measured bandgap value matches well with the black color of the powder sample, much lower than the predicted value of I42d-LiGaSe₂ and experimental value of orthorhombic Pna2₁-LiGaSe₂ (3.34 eV), which may be attributed to the excess Se during chemical synthesis. By calculating IR vibrational spectrum (Figure 6c), it is found that its highest energy vibration mode is less than 322 cm⁻¹, infering that the IR absorption edge of $I\overline{4}2d$ -LiGaSe₂ is longer than 12 µm, which can cover two atmospheric transparent windows (3-5, 8-12 µm), and can be used as potential IR NLO material applied in mid-IR regions. And the Raman spectrum of I42d-LiGaSe₂ single crystal was measured to further confirm the chemical composition and crystal structure. As shown in Figure 6d, the strong absorption peak at 165 cm⁻¹ can be assigned to the characteristic vibration of Ga-Se bonds, and the absorption peak below 100 cm⁻¹ primarily corresponds to Li-Se vibration in I42d-LiGaSe₂. Complete experimental and calculated characterizations further testify the rationality of the predicted structures, which opens new avenue for exploring excellent IR NLO materials by data-driven HT methods.

Why does $I\overline{4}2d$ -LiGaSe₂ has such a large SHG response? To decipher the origin, the electronic structure of $I\overline{4}2d$ -LiGaSe₂ was investigated in detail. As shown in **Figure** 7a, the valence band maximum and conduction band minimum locate at the same G point, illustrating that $I\overline{4}2d$ -LiGaSe₂ is a direct bandgap compound. It is well known that optical properties mainly depend on the electronic states close to the Fermi level. As shown in Figure 7b, the top of valence band is mainly



Figure 6. a) Calculated and experimental powder X-ray diffraction patterns of $I\overline{4}2d$ -LiGaSe₂; b) The powder SHG data for $I\overline{4}2d$ -LiGaSe₂ at 2090 nm laser radiation using classic AGS as reference; c) IR vibrational spectrum of $I\overline{4}2d$ -LiGaSe₂; d) Raman spectrum of $I\overline{4}2d$ -LiGaSe₂.







Figure 7. a) Electronic band structure of $I\overline{4}2d$ -LiGaSe₂ using the HSE06 functional; b) Partial density of state (PDOS) of $I\overline{4}2d$ -LiGaSe₂; c,d) The SHG density maps of occupied and unoccupied orbitals in the VE process of the SHG coefficient tensor d_{15} in $I\overline{4}2d$ -LiGaSe₂.

occupied by Se-4*p* and Ga-4*p*, the bottom of conduction band derives primarily from the Se-4*s*/4*p* and Ga-4*s*. We can conclude that the Ga-Se interactions play a dominant role in determining the bandgap and optical properties of $I\overline{4}2d$ -LiGaSe₂. The SHG-density analysis was also performed to investigate the origin of the SHG response (Figures 7c,d). Since the contribution of VE process in $I\overline{4}2d$ -LiGaSe₂ is predominant to SHG response, only the VE process for the largest SHG coefficient tensor d_{15} in the effective SHG coefficient was analyzed. From Figures 7c,d, we can find that Se atoms contribute to the occupied states.

4. Conclusion

In this work, we utilized machine learning method to realize the rapid prediction of bandgaps of 3887 chemical compositions, of which 1620 samples have bandgaps larger than 2.50 eV. Our reported target-driven paradigm that integrates machine learning, crystal structure prediction, HT compulation and screening, database establishment, and experimental verification has achieved the ability from theoretical design to directed synthesis. Using that, all known structures, five thermodynamically stable and 50 metastable new ternary selenides were predicted successfully from $A^{I}B^{III}$ Se₂ (A^{I} = Li, Na, K, Rb, Cs; B^{III} = Al, Ga) chemical compositions standing out of 325 chemical systems. For $A^{I}AlSe_{2}$ and $A^{I}GaSe_{2}$ (A = Li, Na, K, Rb, Cs), they were characterized by wide bandgap ($E_{\rm g}$ > 2.70 eV) and large SHG coefficient tensor ($|d_{ii}| > 10 \text{ pm V}^{-1}$), respectively. Moreover, $Pna2_1$ -LiGaSe₂, I42d-LiGaSe₂, Fdd2-KAlSe₂, Pna2₁-KAlSe₂, I42d-KAlSe₂, Pna21-RbAlSe2, I42d-RbAlSe2, and I42d-CsAlSe2 were screened out and could be regarded as potential candidates for mid-IR NLO application. The predicted $I\overline{4}2d$ -LiGaSe₂ and I4/mcm-KAlSe₂ were synthesized successfully, which confirms the validity of the paradigm. Via experimental and theoretical evaluation, $I\overline{4}2d$ -LiGaSe₂ exhibits a large SHG response ($\approx 2 \times AGS$) with phase-matching capability and long IR absorption edge (>12 µm) that can cover two important atmospheric windows. Besides, the in-depth mechanism probe strongly demonstrates that the [GaSe₄] polyhedra play a crucial role in the optical performance of $I\overline{4}2d$ -LiGaSe₂. This new research paradigm is also applicable to the discovery of new materials in other fields, such as photovoltaics, ferroelectrics, and piezoelectrics.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

crystal structure prediction, high-throughput computation and screening, machine learning, nonlinear optical material, second harmonic generation response

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