


 Cite this: *Chem. Commun.*, 2025, 61, 5122

 Received 15th January 2025,
 Accepted 3rd March 2025

DOI: 10.1039/d5cc00259a

rsc.li/chemcomm

Unveiling the physical mechanisms underpinning bandgap variations in chalcopyrite crystals (ABX₂) using interpretable artificial intelligence†

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We propose an interpretable AI approach integrating hybrid DFT, symbolic regression, and data mining to predict chalcopyrite (ABX₂) bandgaps. Key factors, including atomic size, molar volume, and electron affinity, are identified, offering insights into bandgap-composition relationship and guiding high-performance materials design.

Ternary chalcopyrite crystals (ABX₂) are essential in various technological applications due to their tunable bandgaps, determined by the selection of A, B, and X elements. Large-bandgap materials, such as ZnSnP₂,¹ are used in nonlinear optics because of the strong nonlinearity and high optical damage thresholds, making them ideal for applications like laser technology and frequency doubling. Moderate-bandgap crystals, like CdGeAs₂,² are widely employed in photovoltaic cells due to their high absorption coefficients, which make them excellent candidates for thin-film solar cells, enhancing solar energy conversion efficiency. Small-bandgap materials, such as CuMnS₂,³ show promise in thermoelectric devices due to their high electrical conductivity and thermoelectric efficiency,^{4,5} enabling effective waste heat recovery and power generation in thermoelectric modules. The broad range of ABX₂ chalcopyrite crystals' applications highlights the importance of precisely targeting specific bandgap values to meet the demands for different technological advancements.⁶ By selecting appropriate combinations of A, B, and X elements, researchers can tailor the properties of these materials to optimize their performance in various fields, from renewable energy to advanced optical

systems. The ability to fine-tune the bandgaps of chalcopyrite crystals underscores their versatility and significance in modern technology. Therefore, models that can rapidly and reliably predict the bandgaps of these materials are highly desirable.

Bandgaps of compounds are typically obtained through experimental measurements,^{7,8} which often require significant time and material resources, especially for large-scale compounds. As a more efficient alternative, density functional theory (DFT) calculations have become effective means for determining the bandgaps of semiconductor materials.^{9–12} However, DFT calculations with standard approximations to the exchange–correlation functional (local density, generalized gradient, and meta-generalized-gradient approximations) often significantly underestimate bandgap values.¹³ On the other hand, the much more accurate many-body perturbation theory method GW is too computationally expensive for intermediate-throughput screening. To achieve good accuracy in bandgap calculations while keeping computational cost not too high, hybrid functionals, such as Heyd–Scuseria–Ernzerhof (HSE06) functional, have been proposed.^{14,15} Despite having moderate computational cost, these methods are still too expensive for high-throughput exploration of materials space containing thousands of candidates.^{16,17} The thriving development of AI has driven the integration of machine learning with theoretical calculations to accelerate the discovery of materials with desirable properties by extracting informative insights from large datasets.^{18,19} For instance, Gladkikh *et al.* trained an alternating conditional expectation (ACE) model to predict the bandgaps of ABX₃ perovskites, and used a support vector machine (SVM) model to determine the gap type.²⁰ Tawfi *et al.* employed feedforward neural network (FNN), SVM, relevance vector machines (RVM), and random forest (RF) models to predict the electronic properties of mixed 2D materials.²¹ However, these models lack interpretability and cannot explain the physical relationship between the predicted bandgap and the chemical composition.^{22–24} The accuracy and interpretability of machine learning models are both crucial for the rational design of materials.^{25,26} In this letter,

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 † Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d5cc00259a>

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possesses a balance between high accuracy and simplicity, thus identifying it as the optimal SISO model. The distribution of deviations between the predicted and calculated G_{HSE} values for this model is shown in Fig. 2(d), with most errors concentrated below 0.2 eV. The components of the optimal SISO model, including its coefficients and importance scores, are collected in Table S4 (ESI[†]). These complex formulas of the model highlight the intricate relationships between the primary features and bandgap.

The most significant descriptor component, d1, has the highest importance score, calculated as the relative increase of fitting RMSE after this component is removed (see ESI[†] for details). It indicates that B elements with larger molar volumes (MVb), and larger atomic radii of atoms at the X site (ARCC) typically correspond to smaller bandgaps in ABX₂ ternary chalcopyrite crystals. A larger MVb results in the expansion of the crystal lattice, which reduces overlap of atomic orbitals, thereby decreasing the bandgap. Larger atomic radii at the X site have a similar effect. Conversely, thermal conductivity of A-site elemental crystal (TCA) results in the increase of band gap in ABX₂. Since A elements are metals at normal conditions, their thermal conductivity is determined by the presence of nearly free electrons. With right ligands these electrons can make strong covalent or ionic bonds, which increases the bandgap. These insights demonstrate that the SISO model can effectively unravel the underlying physical mechanisms governing the properties of chalcopyrite crystals.

SISO aids in identifying critical descriptor components by selecting important primary features and feature combinations relevant to G_{HSE} values. However, it does not directly elucidate which combinations of features are likely to result in too low or too high bandgap. To deepen our understanding of the underlying mechanisms and the significance of primary features, we employ a modified version of SGD approach.³⁰ Here, only the primary features from the SISO model and SISO-predicted G_{HSE} values are used for SGD analysis.

The best subgroups found are shown in Table S5 (ESI[†]), along with the degenerate propositions. The degeneracy is determined by the condition that the number of common data points in the original subgroup and the subgroup obtained by replacing a proposition with another one is greater than 99% of the larger of the two subgroups. The selector of the best subgroup that minimizes G_{HSE} with cutoff 1 eV (*i.e.*, under condition $G_{\text{HSE}} < 1$ eV) is defined as follows: (ARCC ≥ 98 pm), (EAa ≤ 125.6 kJ mol⁻¹), (EAa ≥ 53.7 kJ mol⁻¹), and (MVb ≥ 11.93 cm³ mol⁻¹). The subgroup contains ~24% of the whole dataset samples (Fig. 3a). The selector is well consistent with the SISO model, indicating that larger ARCC and MVb lead to smaller G_{HSE} . This is explained by reduction of atomic orbital overlap when the lattice is expanded due to larger volume of the unit cell. On top of this, SGD reveals that the electron affinity of atom A is an important feature that controls whether bandgaps are lower than 1 eV. In particular, the electron affinity should not be too low (EAa ≥ 53.7 kJ mol⁻¹) or too high (EAa ≤ 125.6 kJ mol⁻¹). The latter condition is degenerate with AWa ≤ 112.41 a.m.u. and ENa ≤ 2.20 . Lowering the cutoff to 0.5 eV results in the best subgroup (AWb ≥ 72.64 a.m.u.) AND (TCA < 120 W m⁻¹ K⁻¹) AND (IEc ≤ 999.6 kJ mol⁻¹). The first proposition is degenerate with

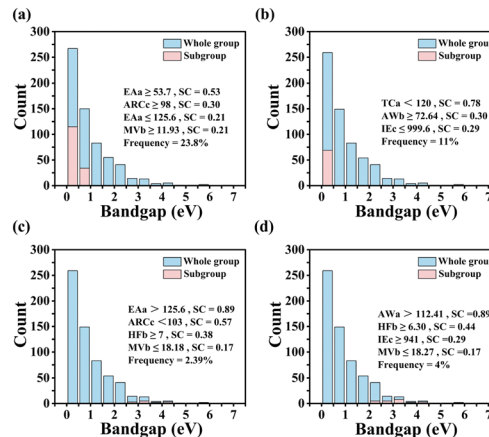


Fig. 3 Exploration of physical insights into the SISO model. The bandgap distribution for the whole dataset, and the subgroups selected by SGD: (a) and (b) The results of minimizing the bandgap with the cutoff smaller than 1 and 0.5 eV, respectively. (c) and (d) The results of maximizing the bandgap of crystals greater than 2.5 and 2 eV, respectively.

MVb ≥ 13.65 cm³ mol⁻¹, which is similar to the proposition MVb ≥ 11.93 cm³ mol⁻¹ in case of a 1 eV cutoff, indicating that a larger size of atom B consistently leads to a smaller bandgap in ABX₂. The proposition TCA < 120 W m⁻¹ K⁻¹ is also consistent with a straightforward interpretation of the SISO model. Lower thermal conductivity of elemental A metals implies more tightly bound and localized electrons that do not form strong bonds. The proposition IEC ≤ 999.6 kJ mol⁻¹ rules out X = N and P, which could make strong covalent bonds with A, resulting in increased bandgap.

The selector for the best subgroup that maximizes bandgaps above 2 eV is defined as follows: (AWa > 112.41 a.m.u.), (HFb ≥ 6.30 kJ mol⁻¹), (MVb ≤ 18.27 cm³ mol⁻¹), and (IEc ≥ 941 kJ mol⁻¹). Increasing the cutoff to 2.5 eV yields best subgroup (ARCC < 103 pm), (EAa > 125.6 kJ mol⁻¹), (HFb ≥ 7 kJ mol⁻¹), and (MVb ≤ 18.18 cm³ mol⁻¹). Consistently, these subgroups contain conditions opposite to those for the subgroups with smaller gaps. A smaller atomic radius of X and a smaller molar volume of B result in shorter interatomic distances, improving orbital overlap and therefore increasing bandgap. The degenerate propositions AWa > 112.41 a.m.u. and EAa > 125.6 kJ mol⁻¹ select only one element (Au), whose high electron affinity makes possible formation of strong covalent bonds with neighboring atoms. Similarly, degenerate propositions HFb ≥ 7 kJ mol⁻¹ and EAb ≥ 42.5 kJ mol⁻¹ select atoms that can form strong localized bonds, resulting in larger gap (Table S5, ESI[†]).

Relying solely on elemental and atomic features, the SISO model enables us to predict the bandgap for a wide array of chalcopyrite crystals. We predicted the G_{HSE} values for 506 new chalcopyrite crystals, and the results are shown in Fig. 4. Based on the high-throughput screening results, we have identified chalcopyrite materials with bandgaps in a range suitable for tandem solar cell and other applications.^{31,32} In Table S6 (ESI[†]) we list 43 materials with direct HSE06 bandgaps in the range 0.6–2 eV.

In summary, we have developed a unified model that quantitatively describes bandgap variations in chalcopyrite crystals by



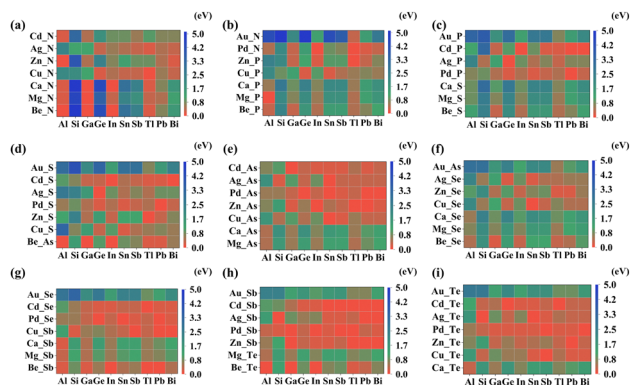


Fig. 4 High-throughput screening results for chalcopyrite crystal bandgaps using SISSO. The horizontal axis displays the type of B-site elements, while the vertical axis displays the combined types of A-site and X-site elements, denoted as "A_X".

integrating HSE06 calculations with AI. This model not only accurately describes composition-bandgap relationship, but also elucidates the underlying physical mechanisms responsible for these variations. Using data mining approach SGD, we identified combinations of features that result in a reduction or an increase of bandgap. SGD finds that size of atom X, molar volume of elemental B crystal, and electron affinity of atoms A and B are important for maximizing or minimizing the gap. The geometric features describe orbital overlap, which directly affects the bandgap. The electron affinity describes the ability of atoms form stronger covalent bonds with neighboring atoms, which leads to higher bandgaps. These findings underscore the transformative potential of interpretable AI algorithms in paving new paths for the rational design of high-performance materials.

This work was financially supported by the National Key R&D Program of China (2023YFA1506902, 2022YFA1505500), National Natural Science Foundation of China (22302173), and the Fundamental Research Funds for the Central Universities. The development of the subgroup discovery method was supported by Russian Science Foundation, grant number 24-13-00317.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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