

Supporting Information

Open-Source DFT Calculations of Electronic Structure to Understand Bonding in Solids

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S1. Procedure for Electronic Structure and PDOS Data Generation

This section provides a detailed explanation of the steps involved in the PDOS and band structure calculation flowchart, as illustrated in Figure 2 of the manuscript.

S1.1. ICSD - Initial Structural Data

The process begins with going to the Inorganic Crystal Structure Database (**ICSD**) website to get the raw structural data by downloading Crystallographic Information Files (**CIFs**) which include detailed information about atomic positions, lattice parameters, and symmetry properties essential for simulation preparation. Other open source options for crystallographic data include the Crystallography Open Database^{1,2} (www.crystallography.net) and the Materials Project³ (www.materialsproject.org). The data used as input structures can be high-quality, experimentally measured under atmospheric pressure and at room temperature, though some differences will be present when comparing to DFT simulations performed at 0 K. Using visualized CIF files⁴, we can examine the structural properties such as atomic arrangement, bond length, symmetry, etc. before running calculations. VESTA⁵ (open source: www.jp-minerals.org) , XCrySDen⁶ (open source: www.xcrysden.org), and CrystalMaker⁷ (www.crystalmaker.com) are useful graphical software for this purpose. XCrySDen is especially advantageous for Quantum ESPRESSO users because it supports direct and easy opening of input and output files. Additionally, it serves as an intermediary tool to convert input and output files into formats compatible with other graphical software.

S1.2. vc-relax: Structural Optimization

The experimental structural data from the ICSD requires subsequent geometry optimization to reach the lowest energy state and align with DFT's force conditions and internal energy expectations for computational accuracy. Variable cell (vc) structural relaxation allows for iterative refinement of geometrical atomic positions and lattice configuration to minimize internal stress and forces. The optimized atomic positions and lattice parameters in the vc-relax output file becomes the starting point for further electronic structure calculations.

To run a vc-relax calculation, the following components are required: PSP files, pw.x executable file, runscript, and input file. **pw.x** is the main QE tool for plane-wave calculations, including vc-relax. It optimizes atomic positions and lattice parameters to minimize the total energy of lattice configuration. The **runscript** manages pw.x execution, input/output flow for multiple calculations. It is an essential file while running calculation on computing clusters. Figure S1 illustrates an example **vc-relax QE input file**. Each separate section, denoted with an ampersand (&), controls a different part of the calculation.

```

a) &CONTROL
    calculation = 'vc-relax',
    prefix = 'Si',
    pseudo_dir = './',
    outdir = './',
    etot_conv_thr=1.D-7,
    forc_conv_thr=2.D-6,
    nstep=150,
/
b) &SYSTEM
    ibrav = 2,
    celldm(1) = 10.26221 ,
    nat = 8,
    ntyp = 1,
    ecutwfc = 40,
    ecutrho = 320,
    occupations = 'smearing',
    smearing = 'gaussian',
    degauss = 0.02,
    input_dft = 'WC',
/
c) &ELECTRONS
    electron_maxstep = 150,
    diagonalization = 'david',
    conv_thr = 1.0d-7,
    mixing_beta = 0.20,

```

```

d) /
  &IONS
  /
  &CELL
    press = 0.0,
  /
  ATOMIC_SPECIES
  Si 28.0855 si_pbe_v1.uspp.F.UPF
  ATOMIC_POSITIONS (crystal)
  Si   0.125  0.125  0.125
  Si   0.125  0.625  0.625
  Si   0.625  0.125  0.625
  Si   0.625  0.625  0.125
  Si   0.875  0.375  0.375
  Si   0.875  0.875  0.875
  Si   0.375  0.375  0.875
  Si   0.375  0.875  0.375
f) K_POINTS {automatic}
  10 10 10 0 0 0

```

Figure S1. An example of a variable cell structural relaxation input file for Si.

To complement the definitions provided by Quantum Espresso, in the next few sections a focus is placed on describing the input parameters that ultimately govern electronic band structure calculations workflow. The following discussion outlines the key parameters and their roles in the setup:

a) &CONTROL

- **calculation**: defines the type of calculation. Here, “vc-relax” means the calculation optimizes both lattice parameters and atomic positions at the same time (vc is variable cell).
- **prefix**: A label used to name output files, here set as 'Si' for silicon. This parameter helps to organize files under a common prefix.
- **pseudo_dir**: Directory of pseudopotential files.
- **outdir**: Directory in which output files will be saved.
- **etot_conv_thr** and **forc_conv_thr**: Convergence thresholds for total energy and atomic forces, respectively, defining the accuracy criteria. It means the calculation will stop iterating once the change in total energy between steps falls below the convergence threshold limit.
- **nstep**: Maximum number of iterations for the relaxation process. It is a restricting parameter to the relaxation iterations. If the convergence occurs earlier, the calculation will be stopped.

b) &SYSTEM

- **ibrav**: defines which of the 14 unique Bravais lattice types applies to the crystal in the QE input file, minimizing input complexity. For example, ibrav = 2 represents a face-centered cubic (FCC) lattice. With a specified ibrav value, QE automatically uses the related lattice vectors (\mathbf{a} , \mathbf{b} , and \mathbf{c}) and angles between them (α , β , γ).
- **celldm()**: defines the size of unit cell in Bohr units. It is one of the key parameters which determines the size for the overall crystal structure.

- **nat and ntyp** : gives the total number of atoms and the number of unique atomic species in the unit cell, respectively.
- **ecutwfc** and **ecutrho**: control the wavefunction and charge density cutoff energies. The cutoff energy decides which planewaves are included in the basis set by controlling the kinetic energy upper limit. **ecutrho** is typically between 4-12 times larger than **ecutwfc** because charge density demands finer detail for accuracy.
- **occupations**: sets the method for electron distribution among energy states in the system. "fixed" for insulators or "smearing" for metals are common ones to improve convergence.
- **smearing**: evenly distributes electrons across energy levels. It applies to the systems with partial band occupancy, mainly metallic systems, leading to smoother and more convergent calculations.
- **degauss**: determines how much partial electron occupancies spread in systems using smearing.
- **input_dft**: defines the exchange-correlation functional used in calculations. "WC" here denotes the Wu-Cohen GGA functional.

c) **&ELECTRONS**

- **electron_maxstep**: sets the limit on the number of calculation rounds for reaching a stable electron configuration within the system.
- **diagonalization**: determines the method for calculating the energy levels of electrons in a system, with speed and accuracy varying by method. "david" is often chosen for accuracy, while "cg" offers greater efficiency.
- **conv_thr**: sets the threshold for the energy change that determines when the calculation stops. The energy change refers to differences in total energy between calculation steps as the electron configuration stabilizes in the material.
- **mixing_beta**: defines the factor for mixing electronic densities between consecutive iterations during self-consistent field (SCF) calculations.

d) **&IONS and &CELL**

The **&IONS** section handles ionic relaxation parameters, with additional parameters for controlling the ion movements if necessary. The **&CELL** section deals with volume and pressure settings. In this example, press=0 sets the external pressure to zero.

e) **ATOMIC_SPECIES** and **ATOMIC_POSITIONS**

- **ATOMIC_SPECIES** lists the atomic types present in the unit cell with their atomic masses and corresponding PSP files.
- **ATOMIC_POSITIONS**, typically derived from ICSD, lists the positions of each atom in the unit cell in fractional coordinates before relaxation.

f) **K_POINTS**: determines how the Brillouin zone is sampled. It can be considered as another parameter to balance speed and precision in calculations. Here, 10 10 10 0 0 0 means a $10 \times 10 \times 10$ grid with no shifts.

S1.3. Band structure and PDOS calculations

This section provides a detailed overview of the band structure and PDOS calculations, using the optimized structure obtained in section 3.2. For a PDOS and band structure calculation, various executables, as summarized in Table S1, are used to perform SCF, NSCF, band structure, and DOS calculations. The workflow starts with **pw.x** to generate electron density and band structure data, followed by **projwfc.x** and **dos.x** for analyzing atomic orbital contributions (PDOS) and total DOS. **bands.x** and **plotband.x** are then employed to create different file formats to facilitate plotting and visualization of the band structure.

Table S1. Overview of programs, inputs, and outputs for electronic structure and DOS calculations

Executable	Input	Output				
pw.x	scf.in	scf.out				
	nscf.in	nscf.out				
	bands.in	bands.out				
projwfc.x	pdos.in	pdos.out	pdos_tot	"filpdos".pdos_atm#N(X)_wfc#M(l)		
dos.x	dos.in	dos.out		dos.dat		
bands.x	bands.in	bands.dat	bands.dat.rap	bands.dat.gnu	bands.out	bands.ps
plotband.x	plotband.in	plotband.out				

S1.3.a. **pw.x:** SCF, NSCF, and Band structure calculations

As explained at the beginning of section 3, the **SCF calculation** determines ground state electron density of a material by iteratively solving the KS equations until convergence. The result of this step is used for consequent calculations. The **Non-Self-Consistent Field (NSCF)** calculation is the next on the list. Without recalculating the electron density, NSCF uses the obtained electron density by the SCF calculation to compute the electronic states at a denser k-point grid, preparing for a higher resolution band structure analysis. **Band Structure Calculation** performed by the same **pw.x** executable, the bands.in step, using the electron density generated from the SCF step, computes the electronic band structure along a path with selected high-symmetry points **in the Brillouin zone** for visualized analysis. The input files for all three calculations are quite similar to those used for vc-relax calculations with some minor difference:

- **nbnd Parameter:** is added to the **&SYSTEM** section which presents the number of electronic states (bands) to be calculated. If the system is insulator, the default value is the number of valence bands (number of electrons divided by two) and if the system is metallic, it should be number of valence bands plus an additional 20% to account for conduction bands.
- **Calculation Mode:** calculation= ‘**scf**’ for SCF file. calculation= ‘**nscf**’ for NSCF file. calculation= ‘**bands**’ for Bands file.

- **k-Point Grid:** a denser k-point grid in the **NSCF file** comparing to scf and vc relax files for a more detailed result. **Bands** calculation, uses a custom k-point path along high-symmetry points in the Brillouin zone to map out the band structure. This k-point path in the reciprocal lattice matches the symmetry of the crystal and use standard labels from crystallography. According to the crystal symmetry of the system under study, the recommended high-symmetry k-point path for that symmetry can be found in the literature^{8,9}.
- **The output files** contain key information for analyzing the electronic properties of materials and performing subsequent calculations. The **SCF output** specifies the converged electron density, total energy, Fermi energy of the system and atomic forces. The **NSCF output** provides detailed eigenvalues and wavefunctions across a denser k-point grid, required for more refined energy bands. The **bands output** gives eigenvalues at each k-point along the high symmetry path in the Brillouin zone. This provides the key dataset for plotting the electronic band structure, and identifying the E_g for insulators and semiconductors. Key information from each output file will be highlighted in Section 4, but all users are encouraged to go through the output log files in greater detail.

S1.3.b. projwfc.x, dos.x: PDOS and DOS calculations

After pw.x calculations (SCF, NSCF, bands), further analysis can focus on density of states with **projwfc.x**, for orbital contributions, and **dos.x**, for the total DOS related to electronic state distribution across energy levels. Both calculations use NSCF output wavefunction and eigenvalues data for processing density of states information. Both **input files** contain basic parameters. The PDOS input defines the output directory (outdir), prefix (prefix), and step size (DeltaE). DeltaE sets the energy increment defining the resolution of energy distribution information. The DOS input includes the energy limits (Emin, Emax), DeltaE, output directory, and filename (fildos).

Projwfc.x calculation result is given by specified **output files**. **pdos.out** can be considered as an overview of **pdos_tot**. In pdos_tot, the total PDOS data for all atoms and orbitals in the unit cell in the specified energy range is included, while in **pdos.out** information about parameters, method, summary of total PDOS values, convergence and warnings are included.

Atomic PDOS by atom and orbital type is stored in files like **filpdos.pdos_atm#N(X)_wfc#M(l)**, where N, X, and l represent the atom number, symbol, and orbital type (s, p, d, f), respectively. These files are generated per atomic wavefunction in the pseudopotential file and are used to plot PDOS for individual atomic orbitals in a material. For example, Si.pdos_atm#1(Si)_wfc#2(p) contains PDOS data for the p orbital ($l=1$) of the Si atom labeled by number 1. Each file is composed of columns arranged as follows:

- **E (eV):** energy of the orbital in eV.
- **ldos(E):** the total DOS for a particular orbital by summing contributions from each orbital component.

- **pdos(E)** Columns: is the DOS projected onto each component. ldos (E) is calculated by summing these pdos(E) values. The order of orbital components columns appears as: p_z-p_x-p_y (for a p-orbital) and d_{z²} - d_{zx} - d_{zy} - d_{x²-y²} - d_{xy} (for a d-orbital).

This means that an **s-orbital pdos** file has three columns, a **p-orbital pdos** file has five columns, and a **d-orbital pdos** file has seven columns. In spin-polarized cases, atoms with unpaired d-orbitals, each **pdos(E)** and **ldos(E)** entry has separate columns for spin-up and spin-down components, doubling the number of columns.

S1.3.c. bands.x, plotband.x

The **bands.x** executable program reads the raw data generated by **pw.x** in calculation = 'bands' mode (section 3.3.a). The **bands.in** file includes information about prefix to align with **pw.x** input files, filband for output naming, and outdir to locate the directory where these data are stored. It formats and reorder the band structure information, producing various output files for visualization.

bands.dat contains the band structure in a format with re-ordered bands suitable for plotting code "plotband.x". **bands.dat.rap** (with symmetry information) contains raw data for custom plotting, **bands.dat.gnu** format prepared for Gnuplot visualization, **bands.ps** plots band structure immediately in PostScript format. **bands.out** is the log file for **bands.x** and includes additional details on calculated properties, summarizing any band properties computed.

S1.4. Data visualization

The PDOS-Band graph can be presented by two-panel setup, with the left panel displaying the band structure using data from **bands.dat.gnu**. The right panel visualizes the distinct density of states contributions from each atom and orbital, using **filpdos.pdos_atm#N(X)_wfc#M(I)** pdos files. In this study, we used open source **XmGrace** package to plot the Bands-PDOS graphs. **XmGrace** is designed specifically for Unix-based systems like Linux, macOS with XQuartz for GUI support or on clusters, for remote users. **XmGrace** is the graphical version of **Grace** which is also developed for Unix-based systems, including Linux and macOS. XmGrace is not available on Windows but it can be run via **Cygwin**.

For Windows users, there are some alternative options like: **OriginPro** which is an advanced licensed software for complicated plotting. Gnuplot^{10,11} is free and works well for plotting these graphs but might be challenging to learn. Matplotlib is python plotting library offering high-quality customizable plots for users with coding background.

S2. Crystal structure and supplemental electronic structure analysis

Table S2 provides an overview of lattice constants and key electronic structure parameters for all seven system of materials. This table highlights differences between experimentally measured and DFT-calculated lattice constants, along with essential electronic properties such as the minimum energy level in the conduction band and the maximum energy level in the valance band, which are fundamental to band structure analysis. While the main article already covers the four primary semiconductor and oxide system, this section focuses on the remaining three complex oxides: PbO, PbTiO₃, and CaCO₃, providing PDOS and band structure analysis, along with unit cell structure and bonding characteristics.

Table S2. A brief review of compounds in this study

Compound	Lattice Constant (Å) ICSD	Lattice Constant (Å) DFT	E _v (eV)	E _c (eV)	E _f (eV)	E _g (eV)
Si	a = b = c = 5.43	a = b = c = 5.74	6.10	6.57	6.33	0.47
GaAs	a = b = c = 5.65	a = b = c = 5.66	7.11	7.48	7.30	0.37
ZnS	a = b = c = 5.41	a = b = c = 5.36	6.98	8.99	8.05	2.01
ZnO	a = b = 3.25, c = 5.21	a = b = 3.24, c = 5.23	8.69	9.35	9.18	0.66
PbO	a = b = 3.98, c = 5.02	a = b = 3.99, c = 5.03	8.49	9.81	9.28	1.32
PbTiO₃	a = b = 3.90, c = 4.15	a = b = 3.87, c = 4.21	10.45	12.14	11.25	1.69
CaCO₃	a = 5.74, b = 4.96, c = 7.97	a = 5.67, b = 4.95, c = 7.93	5.93	10.07	7.50	4.14

PbO (Litharge)

Litharge, also known as lead monoxide (PbO), crystallizes in a tetragonal layered structure. As shown in Figure S.2.a, each lead (Pb) atom is bonded with four oxygen (O) atoms and each oxygen atom is also bonded to four lead atoms under a mixture of ionic and covalent bonding character and equal Pb—O bond lengths of 2.32 Å which is an indicative of strong interaction between the ions. This square planar arrangement creates a layered structure. The lattice parameters for litharge are typically around a =b=3.98 Å° and c = 5.02 Å°. The symmetry of the litharge crystal structure belongs to the centrosymmetric space group P4/nmm, which is known as a high degree of symmetry for tetragonal crystals^{12,13}.

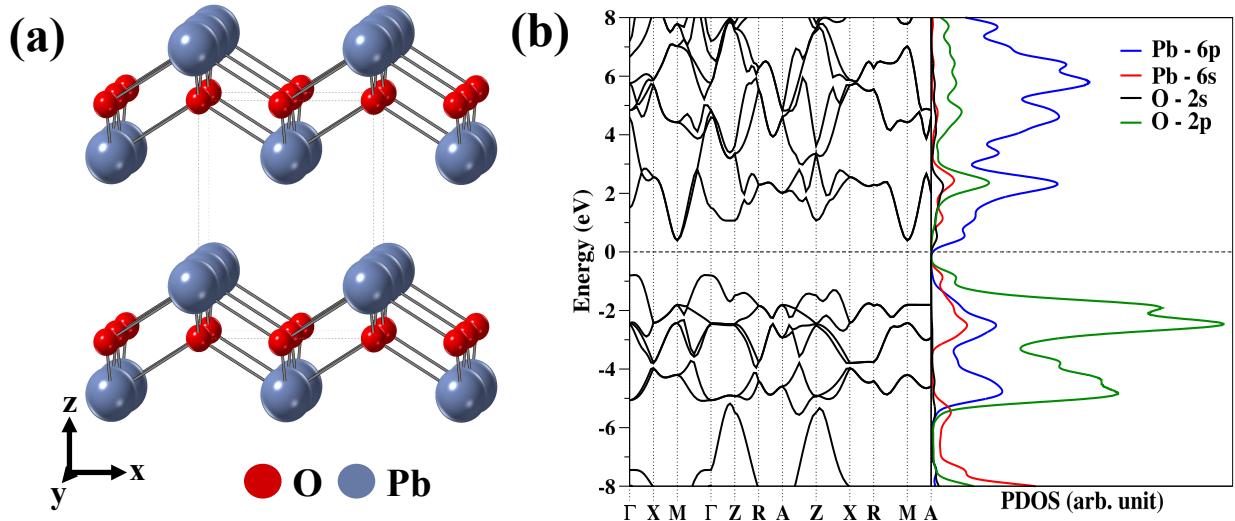


Figure S2. PbO Band structure and PDOS

The band structure of litharge provides insights into the semiconductive behavior of litharge with an indirect E_g , with the VBM and CBM located at the Γ point and the M Point, respectively. The calculated E_g from the graph is approximately 1.32 eV, which is lower than the indirect E_g empirical value of around 1.95 eV¹⁴ due to the typical underestimation of E_g s in DFT calculations. The PDOS plot illustrates that near Fermi level, cationic Pb 6p orbitals are dominantly occupying states in the conduction band region while anionic O 2p orbitals are mainly contributing to the bonding and valence band structure of litharge. In the valence band, the interaction between Pb 6s, Pb 6p, and O 2p states represents a mixed bonding characters in a way that ionic Pb-O bonding, due to charge transfer, is partially balanced by covalent overlap of Pb 6p and O 2p orbitals. In the conduction band, the Pb 6p orbitals play a key role, with some hybridization with O 2p states. Overall, the presence of well-defined peaks of O 2p and Pb 6p is indicative of strong ionic bonding character which can be also an explanation of litharge being the most energetically favorable and thermodynamically stable phase of lead oxide. Besides the dispersive nature of the bands, in the core level of energy, the overlap between Pb and O orbital is an indicative of covalent bonding^{14,15}.

PbTiO₃ Tetragonal ABO₃

PbTiO₃ is a ferroelectric ABO₃ perovskite solid known for its strong polarization. It crystallizes in the polar tetragonal P4mm (99) space group with lattice parameters of $a=b=3.90$, and $c=4.15$ Å. Ferroelectrics are unique materials which possess an internal electric charge (dipole) even in the absence of electric field. Additionally, the direction of this internal dipole can be reversed in the presence of an external electric field^{16–18}. As it is demonstrated in Figure S3.a, the unit cell shows the large Pb cation in the corner and the smaller Ti cation caged in the center by oxygen anions. There are two inequivalent oxygen (O²⁻) sites. In the first site, O²⁻ is coordinated to two equivalent Ti⁴⁺ and two equivalent Pb²⁺ atoms. However, in the second site, O²⁻ is bonded in a distorted single-bond geometry to two equivalent Ti⁴⁺ and four equivalent Pb²⁺ atoms.

Consequently, Ti^{4+} is surrounded by six O^{2-} atoms in an octahedral geometry with $\text{Ti}-\text{O}$ distances ranging from 1.39 to 2.76 Å. Forming a distorted 8-coordinate geometry, Pb^{2+} is bonded to eight O^{2-} atoms with four shorter, 2.55 Å, and four longer, 2.81 Å, $\text{Pb}-\text{O}$ bond lengths. This configuration features the complex bonding environment within the PbTiO_3 structure^{19,20}.

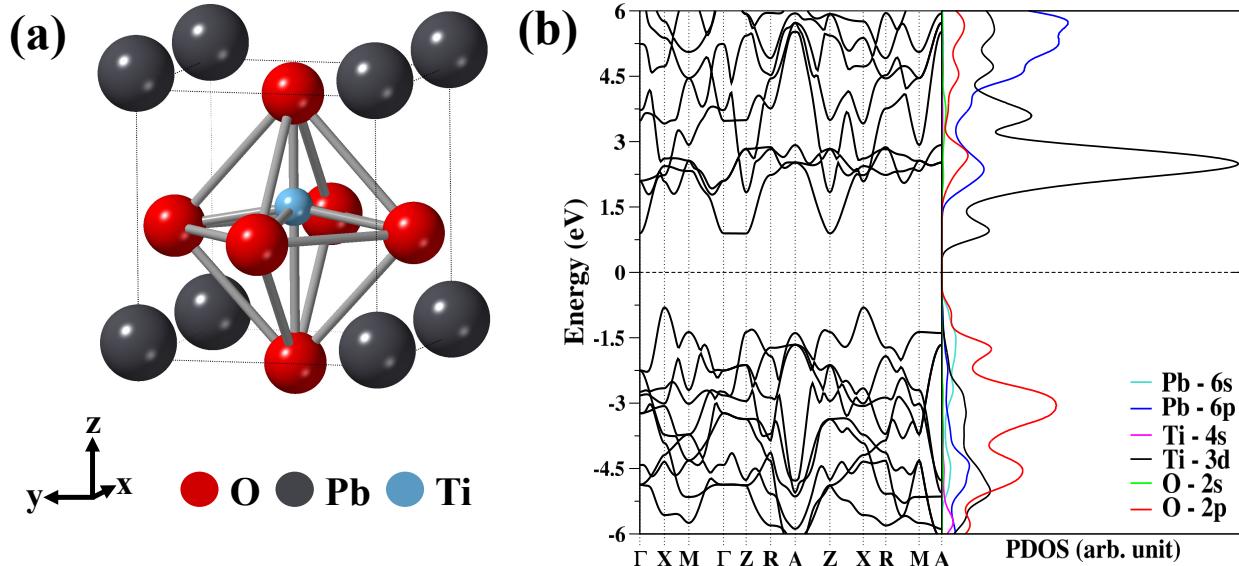


Figure S3. PbTiO_3 (a) Unit cell, (b) PDOS- Band structure

As shown in Figure S3, the tetragonal phase of PbTiO_3 exhibits an indirect E_g with the VBM at the X point and CBM located at the Γ/Z point. The calculated E_g value from the graph is approximately 1.69 eV, which underestimates the experimentally measured E_g (~ 3.4 eV)²¹ due to the reasons previously mentioned. The valence band area is primarily dominated by O 2p states. Closer to VBM area, a strong hybridization of O 2p with the Pb 6s orbitals can be seen. The Ti 3d states also strongly hybridize with both O 2p and Pb 6p states. However, Ti 3d orbitals play the main role in the conduction band region, particularly near the fermi level (CBM area). Pb 6p states also contribute mostly higher up to the conduction band, hybridizing with the surrounding O 2p states. It can be concluded that band structure of PbTiO_3 is largely influenced by the Ti 3d - O 2p hybridization and Pb orbitals play the secondary role, further from the E_g area. The asymmetrical patterns in the band structure plot, especially around the Fermi level in the conduction band region which is coming from the variation in orbital overlap shown in the PDOS plot can be a consequence of the non-centrosymmetric nature of the PbTiO_3 crystal structure. The PDOS plot is also a good guide to find out the origin of the strong polarization and ferroelectricity in PbTiO_3 . Focusing on the $\text{Ti}-\text{O}$ cage surrounded by Pb ions and checking near valence band maximum area in the PDOS plot, reveals the covalent bond nature between both Pb 6p — O 2p and Ti 3d — O 2p states. The ionic core Pb-O repulsion is weakened by the covalent Pb 6p — O 2p bonds, resulting in displacement of Ti ions and lower non-centrosymmetric symmetry state¹⁶.

CaCO₃ (Aragonite)

Calcium carbonate can be found in three primary phases called Calcite (trigonal), Aragonite (orthorhombic) and Vaterite (hexagonal). Here, we look at the characteristics of Aragonite phase with a focus on the electronic band structure and PDOS properties. The primitive cell of Aragonite phase includes 20 atoms whose structure is classified in space group 62 (Pnma) with orthorhombic crystal symmetry. The aragonite phase has an orthorhombic centrosymmetric crystal structure, as shown in the left panel of Figure S4.a, with a layered arrangement where each calcium, carbon, and oxygen atom contribute to forming planar units.

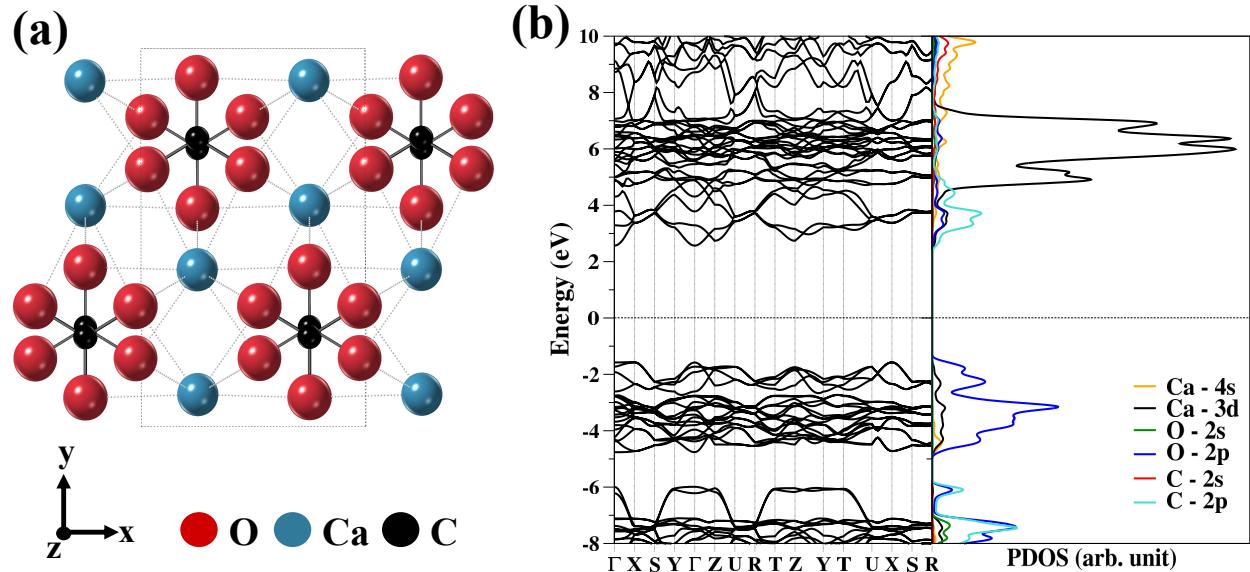


Figure S4. CaCO₃ (a) Unit cell, (b) PDOS- Band structure

Ca atoms are stuffed between carbonate groups, while Ca atoms are located at the center of each carbonate group, forming trigonal planar CO₃ units with oxygen atoms. This creates a stabilized structure bonded by the ionic and covalent interactions between Ca²⁺ ions and the CO₃²⁻ groups, ionic for Ca-O and covalent for the CO₃ unit. In this configuration, there are nine Ca-O and three C-O bonds ranges from 2.38 to 2.53 Å and 1.28 to 1.30 Å, respectively^{22,23}. The experimental lattice parameters are reported to be $a = 5.74 \text{ \AA}$, $b = 4.96 \text{ \AA}$, and $c = 7.97 \text{ \AA}$ and our DFT-optimized results are $a = 5.66 \text{ \AA}$, $b = 4.95 \text{ \AA}$, and $c = 7.93 \text{ \AA}$ which is in a good agreement^{24,25}. In this structure, C⁴⁺ is covalently bonded in a planar trigonal geometry to three O²⁻ atoms forming the carbonate (CO₃²⁻) group. Ca²⁺ ions form a two-layered close packed structure coordinated by CO₃²⁻ groups through ionic bonding. The Ca atoms are situated in distorted tricapped trigonal prism and are nine-coordinated with oxygen atoms. The distortion in the polyhedral structure and high coordination number of oxygen optimizes the stability by minimization of the repulsion between cations (Ca²⁺) and anions (CO₃²⁻).

The electronic energy PDOS and band structure of aragonite show an indirect E_g of 4.14 eV with the effective VBM is degenerate at the Γ and X points and CBM located at the Γ -point, using this level of DFT. In the valence band region, the plot indicates a strong presence of O 2p states with an anionic character, which dominate this area, suggesting that oxygen plays a substantial role in

the bonding within CaCO_3 , particularly in its interaction with carbon and calcium. This is followed by a smaller share of Ca 4s and Ca 3d. The lower energy (more negative) area belongs to a mixture contribution of C 2p and O 2p orbitals and the overlap of states indicates the hybridization of C 2p with O 2p states which creates strong bonding states. In CO_3^{2-} , the C with 4+ oxidation state balances the three oxygens which leads to several resonance structures, delocalization of the electrons and partial double band character. In this situation, the C 2p orbitals are engaged in multiple bonding interactions, leading to the formation of bonding and anti-bonding molecular orbital. In the conduction band, the lowest unoccupied states primarily belong to C 2p orbitals followed by Ca 3d and O 2p overlap with antibonding character. This highlights the significant role of carbon in conduction. The antibonding character of Ca 3d and O 2p overlap implies that electrons in these states weaken Ca–O bonds, affecting stability at higher energy levels. Moving further up in energy, the PDOS shows a prominent peak for the unfilled Ca 3d orbitals and a less pronounced peak of the unfilled Ca 4s states in higher energy area.

S3. Step-by-Step Guide to PDOS and Band Structure Visualization

To plot both the PDOS and band structure in the same figure, as in Figures 3-6 of the main text, we need to create two panels in one figure using XmGrace. The right panel will display the PDOS, and the left panel will show the band structure.

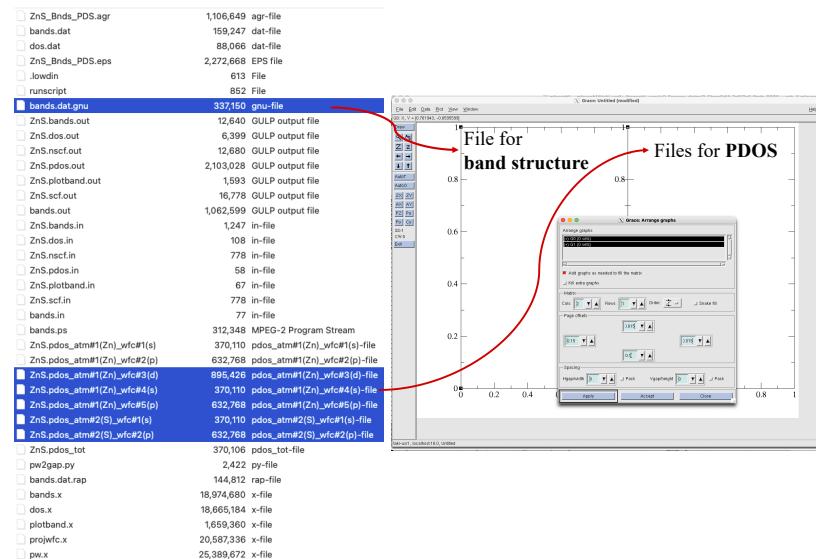


Figure S5. data files used to plot PDOS and band structure.

S.3.1 Arranging PDOS and band structure graphs using input files:

As mentioned earlier in S.1.4, the PDOS-Band graph is presented in a two-panel setup: the left panel displays the band structure using data from bands.dat.gnu, while the right panel shows the projected density of states (PDOS) contributions from each atom and orbital, based on filpdos.pdos_atm#N(X)_wfc#M(l) files (Figure S5).

To organize the panels:

1. Navigate to Edit → Arrange graphs in XmGrace.
2. In the displayed box, you will find all the options required to set the size and spacing for the panels within the figure.

S.3.2. Steps for plotting the band structure using band.dat.gnu:

To begin, we will first focus on the left panel to plot the band structure. For this, we need the related dataset, typically in the form of a **.gnu** file generated from the calculations.

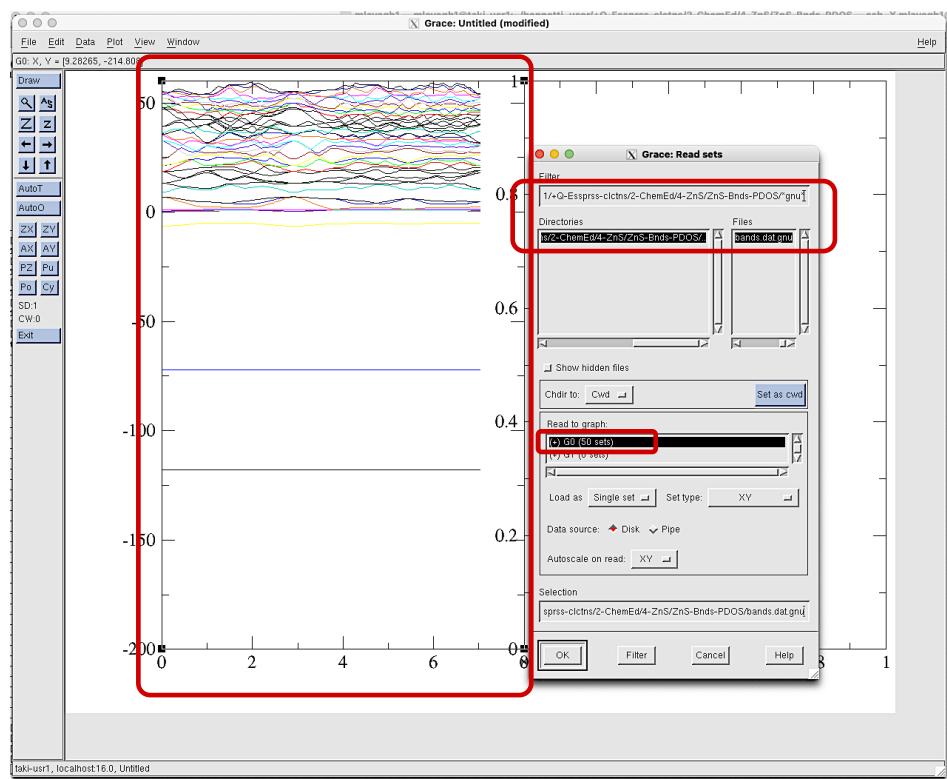


Figure S6. Importing band structure data

Importing the data file:

1. Go to Data → Import → ASCII in XmGrace.
2. In the Filter box, type ***gnu*** to filter the files, so the band.dat.gnu file appears in the Files box (Figure S6).
3. Select band.dat.gnu and click OK.
4. The data for the band structure will now be displayed in the G0 plot box (left panel).

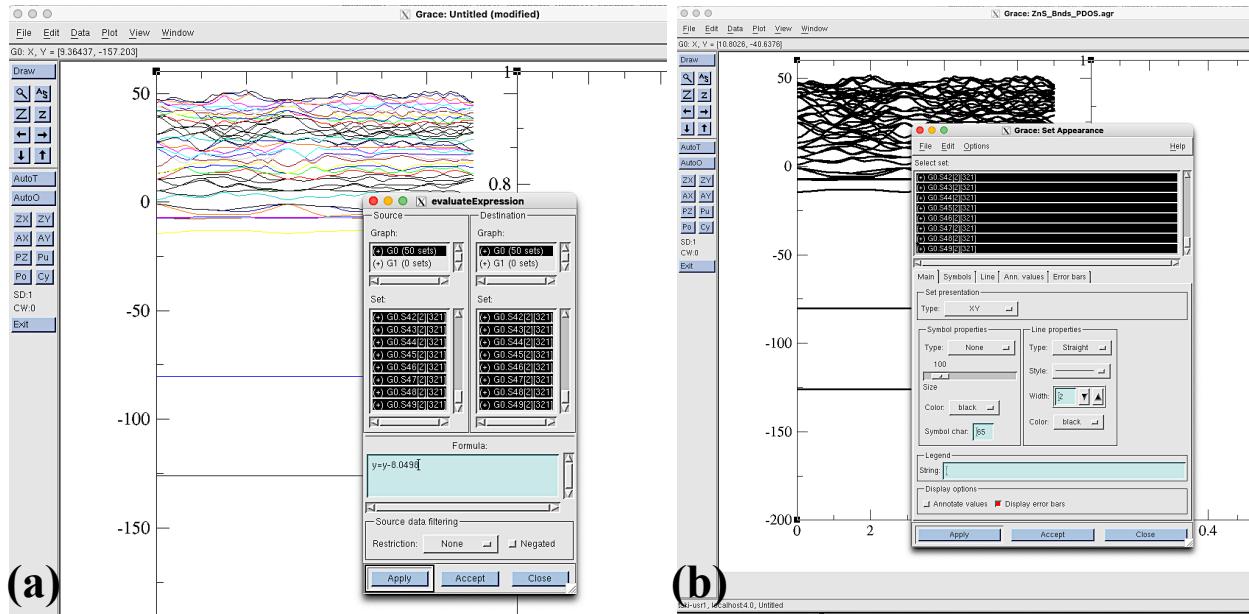


Figure S7. (a) Zero the Fermi level. (b) Editing graph's appearance.

Before plotting the band structure, ensure you have the Fermi energy value from the **scf.out** file. To find this:

Run the following command in the terminal:

```
grep "Fermi" ZnS.scf.out
```

The output will look something like this:

the Fermi energy is 8.0498 eV.

Zero the Fermi level in the plot (Figure S7.a)

Follow these steps:

1. Go to **Data** → **Transformations** → **Evaluate Expression** in xmgrace.
2. Select **all datasets** in both the **Source** and **Destination** boxes.
3. In the **Formula** box, type:

$$y = y - E_f$$

4. Replace E_f with the actual Fermi energy value (e.g., 8.0498).

5. Click **Apply**.

Avoid clicking Apply multiple times, as this will shift the bands repeatedly.

Enhancing the graph's appearance (Figure S7.b)

- Adjusting the color and size of the bands:

1. Click on any part of the graph where the bands are visible to open the “Set Appearance” window
2. In the “Select Set” box, select **all datasets** to apply the changes to all bands.
3. In the **Main** → **Line properties** section:

4. Set the **width** to 2.
5. Change the **color** to **black**.
6. Click **Apply** to update the figure.

The changes will be applied immediately and reflected in the graph.

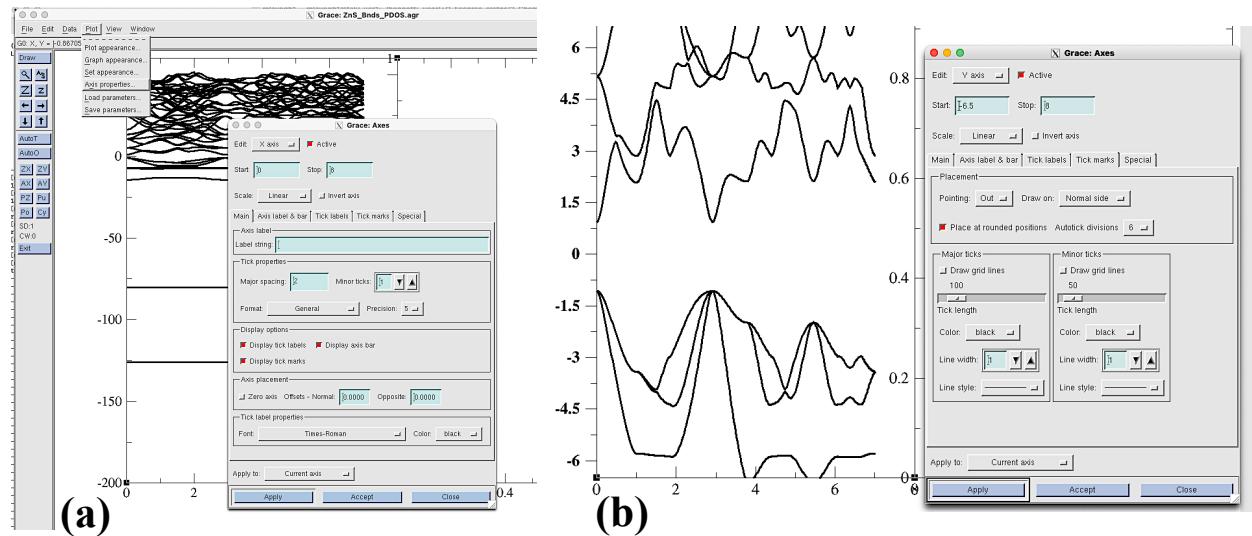


Figure S8. (a) Axes properties, (b) Setting the energy range on Y-axis.

Axes Properties (Figure S8)

To refine the **y-axis** appearance, follow these steps:

Go to **Plot → Axis Properties** and adjust the **y-axis**:

1. **Main Window:** Start = -6.5, Stop = 8, Label = Energy (eV), Major spacing = 1.5, Font = Times Bold.
2. **Axis Label & Bar:** Font = Times-Bold, Char size = 175.
3. **Tick Marks:** Pointing = **Out**, Draw on = **Normal side**.
4. Click **Apply**.

Instructions to Label the X-Axis on the Band Structure Plot (Figure S9)

1. Go to **Plot → Axis Properties** from the top menu.
2. Select **X Axis** and navigate to the “**Special**” tab.
3. For the “**Special ticks**” select: “**Tick marks and labels**”
4. In the Tick Location - Label section:
 - Use the **plotbnd.out** file to enter the x-coordinates of your k-points under Tick Location as guided in Figure S9.a,c.
 - Label each k-point (Γ , X, etc.) based on the **ZnS.bands.in** file. (shown in Figure S9.b,c)
 - Ensure the number of ticks matches the number of high-symmetry points in your k-path.
 - The **number of user ticks to use** should be equaled to the number of high-symmetry point which here is 12.

- Set the **Stop value** to the final k-point.
(For ZnS, use 7.0316)
- Click **Apply** to finalize the changes

Using gridlines to highlight high-symmetry k-points

As shown in Figure S.9.d, we can highlight high-symmetry k-points for better band structure visualization.

- Go to “**Tick marks**” tab
- Enable **Draw Grid Lines under Major Ticks** and adjust line width/color.
- Click **Apply**.

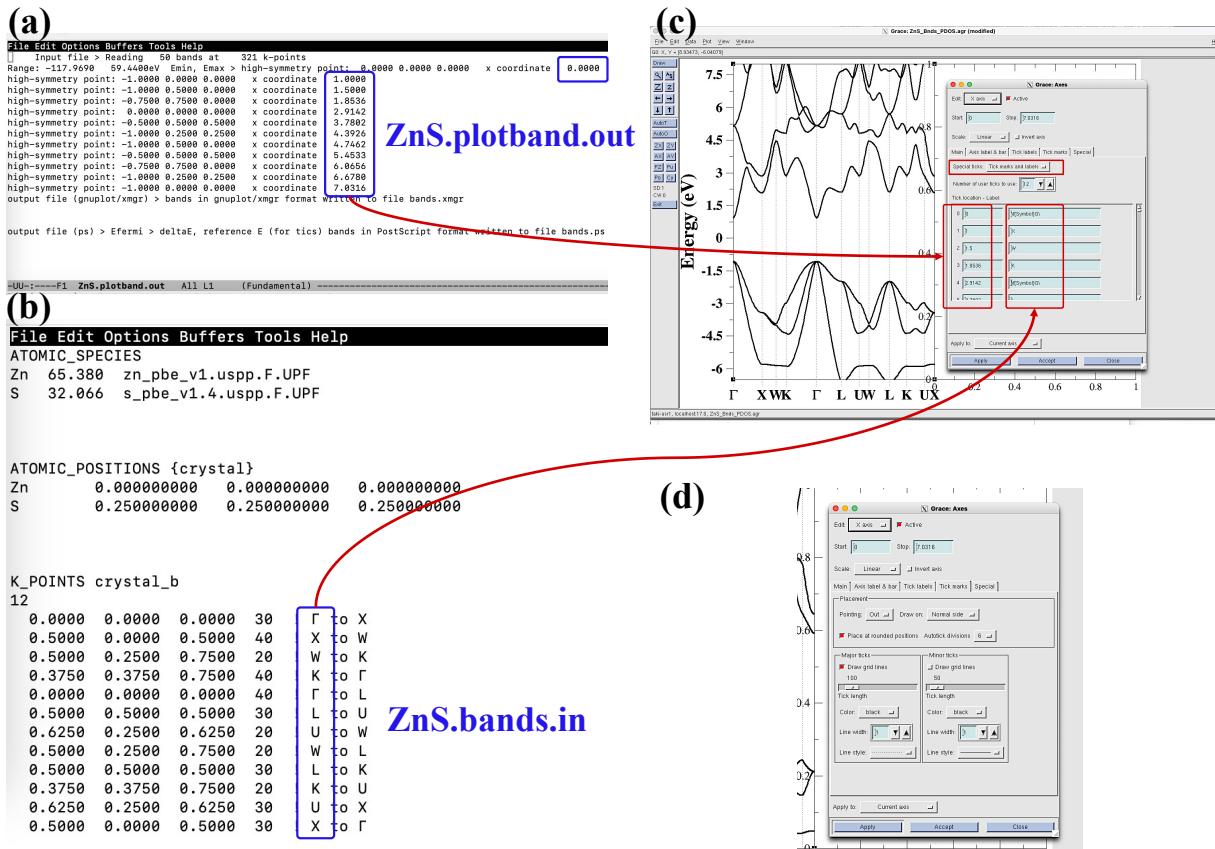


Figure S9. (a) plotband.out file, (b) ZnS.bands.in file, (c) Label the X-Axis on the band structure plot, (d) draw grid lines on high-symmetry k-points.

S.3.3. Plotting the PDOS on the right panel:

We now shift to the right panel to plot the PDOS, following similar steps used for the band structure plotting:

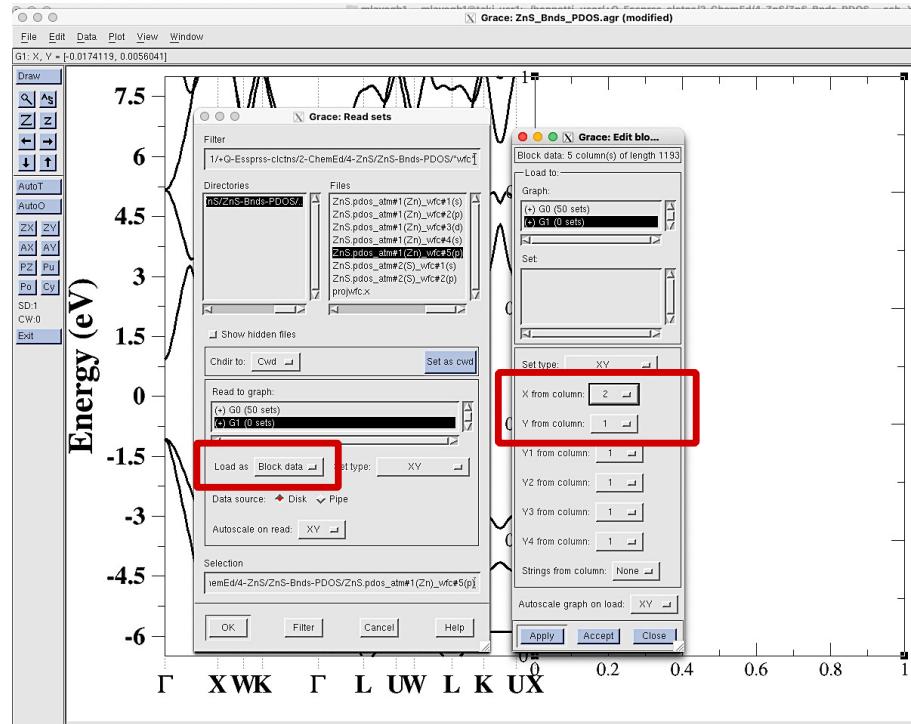


Figure S10. Importing orbital wavefunction data for plot PDOS (right panel)

1. To import the data files which are orbital wavefunctions here:

Data → Import → ASCII

In the Filter box, type ***wfc*** to display all wavefunction files.

2. Ensure data files are loaded as **Block Data** before transferring. (as demonstrated in Figure S10)

3. Load Data for Each Orbital:

4. Start with the Zinc p orbital, select the file, and click OK.

5. In the Edit Block Data window (as demonstrated in Figure S10):

Set the X-axis to column 2 (density).

Set the Y-axis to column 1 (energy).

7. Click Apply.

6. Repeat this process for all other orbital wavefunctions to be plotted.

7. Zero the Fermi Level: Repeat the same steps used for band structure:

Data → Transformations → Evaluate Expression.

Select all datasets in both Source and Destination boxes.

In the formula box, type: $y = y - E_f$, using the Fermi energy (e.g., 8.0498 eV).

Click Apply.

Editing PDOS Curves and Legends (Figure S11)

1. Label PDOS Curves (Figure S11.a):

- Click on the PDOS curves to open the Set Appearance box.

- Navigate to Main → Legend: String and type the orbital name (here: S – 3p).

2. Edit Legend Box (Figure S11.b)

- Go to Plot → Graph Appearance → **Leg. Box** and **Legends** tabs
 - Customize the legend box (font type, size, color, frame size, line, etc.) using the available options.
3. Edit Axes Properties:
- Similar to the band structure plot, go to **Plot → Graph Appearance** to adjust the axis settings.

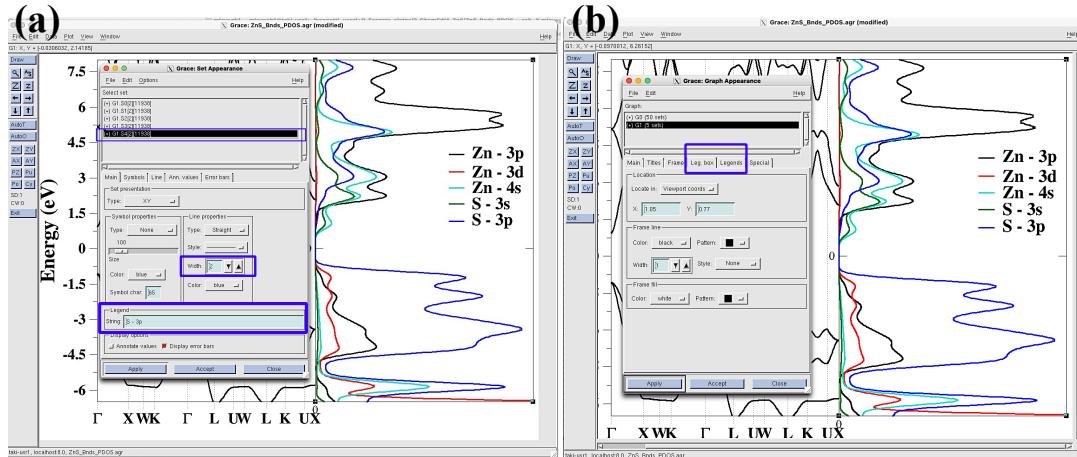


Figure S11. Editing PDOS curves' appearance and legends. (a) Labeling curves (b)Editing legend box.

Drawing a Reference Line at Energy = 0

As seen in all PDOS and band structure plots, a line is drawn at **Energy = 0**, representing the Fermi level (**E_f**), to make it easier to analyze the region near the Fermi energy.

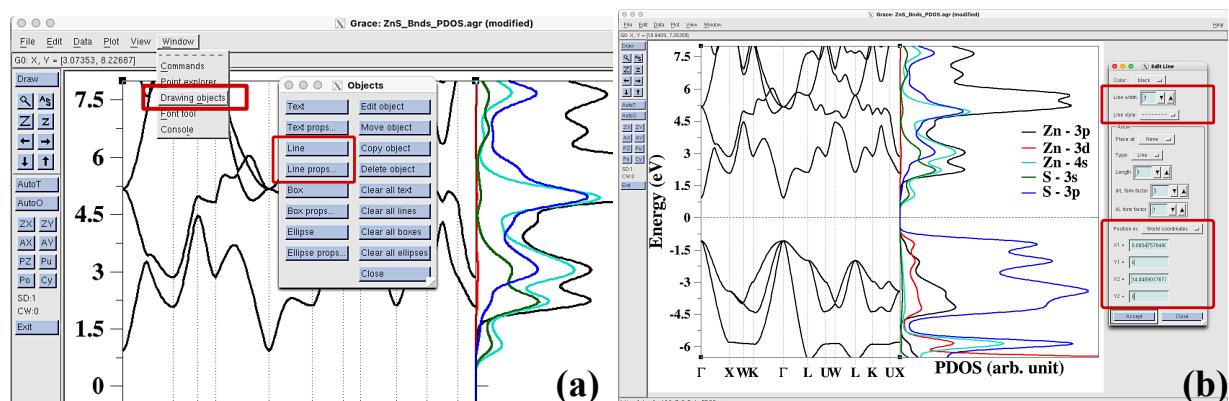


Figure S12. (a) Drawing a reference line at Fermi energy (b) Editing line properties

Steps to Draw the Line (Figure S12):

1. Go to **Window → Drawing Objects → Line**.
2. Draw a horizontal line at **Energy = 0**.

3. Click on the line to open the **Edit Line** box.
 - o Adjust the **placement** and **coordinates** to ensure it aligns with **Energy = 0**.
 - o Customize the **line style**, **color**, and **size** as needed.

Click **Apply** to finalize the line placement.

S.3.4. Saving the Plot as a High-Quality Image (Figure S13)

After completing the plot and saving the main file in “.agr” format, follow these steps to export the image in high quality:

1. **Set Up Printing:** Go to **File → Print Setup** to configure the output settings.
2. **Save as EPS Format:**
 - o Save the file in **EPS (Encapsulated PostScript)** format.
 - o EPS files can be easily converted to **PDF** format, ensuring high resolution suitable for publications or presentations.
3. **Export the Plot:** Go to **File → Print**.

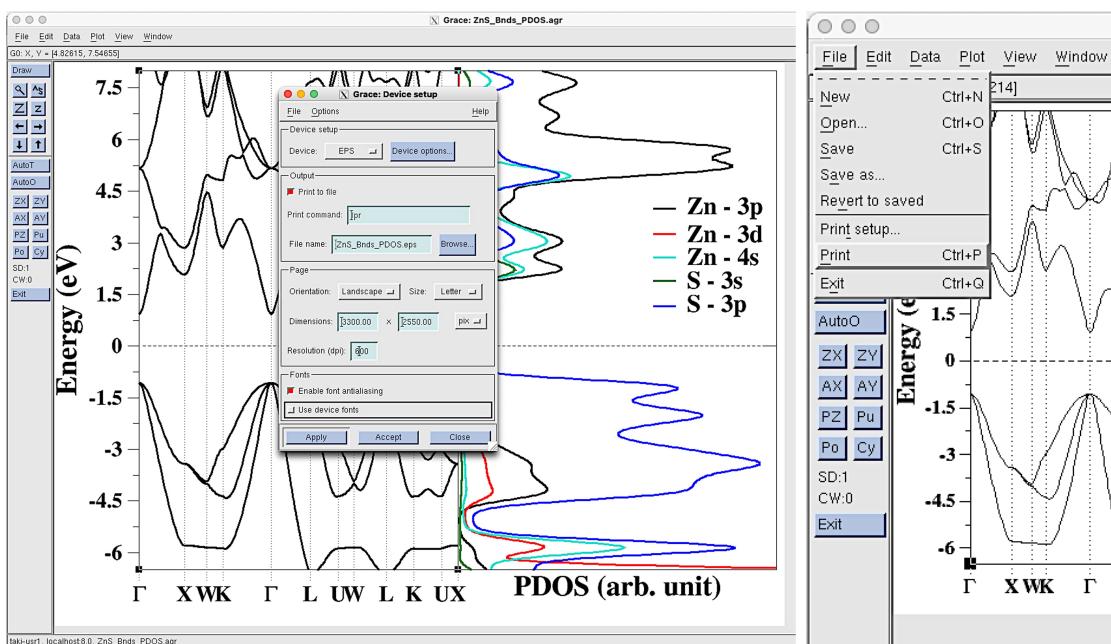


Figure S13. Saving the plot as a high-quality image

S4. Input File Set for PDOS and Band Analysis per Material System

This section presents the input files and their contents for the 7 material systems analyzed in this study. A sample input file set for Si is included to inspire readers to access the complete dataset in the linked open-access digital repositories Zenodo and GitHub and reproduce the calculations.

S4.1. scf input file for Si:

```
&CONTROL
  calculation = 'scf',
  pseudo_dir = './'
 outdir = './temp',
prefix = 'Si',
etot_conv_thr = 1.D-7,
forc_conv_thr = 2.D-6,
nstep = 100,
/
&SYSTEM
  ibrav = 2,
  celldm(1) = 10.27974,
  nat = 2,
  ntyp = 1,
  nbnd = 30,
  ecutwfc = 40,
  ecutrho = 320,
  occupations = 'smearing',
  smearing = 'gaussian',
  degauss = 0.005,
  input_dft = 'wc',
/
&ELECTRONS
  electron_maxstep = 150,
  diagonalization = 'david',
  conv_thr = 1.0d-7,
  mixing_beta = 0.2,
/
&IONS
/
&CELL
  press = 0.0,
/
ATOMIC_SPECIES
Si 28.0855 si_pbe_v1.uspp.F.UPF

ATOMIC_POSITIONS {crystal}
Si      0.000   0.000   0.000
```

```

Si      0.250  0.250  0.250

K_POINTS {automatic}
10 10 10 0 0 0

```

S4.2. nscf input file for Si:

```

&CONTROL
  calculation = 'nscf',
  pseudo_dir = './',
 outdir = './temp',
  prefix = 'Si',
etot_conv_thr=1.D-7,
forc_conv_thr=2.D-6,
nstep=100,
/
&SYSTEM
  ibrav = 2,
  celldm(1) = 10.27974,
  nat = 2,
  ntyp = 1,
  nbnd = 100,
  ecutwfc = 40,
  ecutrho = 320,
  occupations = 'smearing',
  smearing = 'gaussian',
  degauss = 0.005,
  input_dft='wc',
/
&ELECTRONS
  electron_maxstep = 150,
  diagonalization = 'david',
  conv_thr = 1.0d-7,
  mixing_beta = 0.2,
/
&IONS
/
&CELL
  press = 0.0,
/
ATOMIC_SPECIES
Si  28.0855  si_pbe_v1.uspp.F.UPF

ATOMIC_POSITIONS {crystal}
Si      0.000  0.000  0.000
Si      0.250  0.250  0.250

```

```
K POINTS {automatic}
10 10 10 0 0 0
```

S4.3. bands input file for Si:

```
&CONTROL
  calculation = 'bands',
  pseudo_dir = './',
  outdir = './temp',
  prefix = 'Si',
  etot_conv_thr=1.D-7,
  forc_conv_thr=2.D-6,
  nstep=100,
/
&SYSTEM
  ibrav = 2,
  celldm(1) = 10.27974,
  nat = 2,
  ntyp = 1,
  nbnd = 45,
  ecutwfc = 40,
  ecutrho = 320,
  occupations = 'smearing',
  smearing = 'gaussian',
  degauss = 0.005,
  input_dft='wc',
/
&ELECTRONS
  electron_maxstep = 150,
  diagonalization = 'david',
  conv_thr = 1.0d-7,
  mixing_beta = 0.2,
/
&IONS
/
&CELL
  press = 0.0,
/
ATOMIC_SPECIES
Si 28.0855 si_pbe_v1.uspp.F.UPF
```

```

ATOMIC_POSITIONS {crystal}
Si      0.000  0.000  0.000
Si      0.250  0.250  0.250

K_POINTS crystal_b
12
 0.0000  0.0000  0.0000  30 ! Γ to X
 0.5000  0.0000  0.5000  40 ! X to W
 0.5000  0.2500  0.7500  20 ! W to K
 0.3750  0.3750  0.7500  40 ! K to Γ
 0.0000  0.0000  0.0000  40 ! Γ to L
 0.5000  0.5000  0.5000  30 ! L to U
 0.6250  0.2500  0.6250  20 ! U to W
 0.5000  0.2500  0.7500  20 ! W to L
 0.5000  0.5000  0.5000  30 ! L to K
 0.3750  0.3750  0.7500  20 ! K to U
 0.6250  0.2500  0.6250  30 ! U to X
 0.5000  0.0000  0.5000  30 ! X to Γ

```

S4.4. dos input file for Si:

```

&dos
prefix='Si'
outdir='./temp/'
Emin = -20.00,
Emax = 20.00,
DeltaE = 0.015,
fildos = 'dos.dat'
/

```

S4.5. pdos input file for Si:

```

&projwfc
outdir='./temp/'
prefix='Si'
DeltaE=0.015,
/

```

S4.6. bands input file for Si:

```
&bands
  prefix = 'Si'
  filband = 'bands.dat'
  outdir = './temp',
/
```

S4.7. plotband input file for Si:

```
bands.dat
-20.00 20.00
bands.xmgr
bands.ps
6.3300
1.00, 6.3300
```

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