Supporting information for

High-performance lead-free quaternary antiperovskite photovoltaic candidate Ca_6N_2AsSb

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Many-body perturbation theory calculations:

In this report, we used Quantum ESPRESSO v7.1[1] and YAMBO v5.1.0[2] to study the electronic and optical properties of quaternary antiperovskite Ca_6N_2AsSb. The whole calculation can be divided into two steps. In the first step, the structure of Ca_6N_2AsSb is relaxed until the force is less than 10^{-4} Ry. YAMBO works only with Norm-conserving pseudopotentials, thus the scalar-relativistic norm-conserving pseudopotentials pseudo-dojo[3] is used for Quantum ESPRESSO PBE calculations, while the fully-relativistic ones are used for SOC calculations. The pseudo-dojo pseudopotentials suitable for Quantum ESPRESSO is directly download from the website with the recommended standard accuracy. For the SCF calculation, the ecutwfc cutoff of 100 Ry and energy convergence of 10^{-8} Ry are set, the automatic K points 5*5*2 is used to sample the Brillouin zone. For the NSCF calculation, 300 bands are used and denser K points 10*10*5 are used. At the end of NSCF calculation, the database for YAMBO code is converted by the p2y preprocess tool. In the second step, we first converged the optics in the RPA approximation, focused on the parameters of BndsRnXd, NGsBlkXd and the k-points. To speed up the convergence with k-points, a double-grid approach is employed,[4] that is, a much denser k-points of 21*21*10 is re-calculated and the database is re-converted by p2y. After we converged the number of k-points, bands and G-vectors in optics, we started the GW calculation, for the G_0W_0 calculation, we converged the BndsRnXp, NGsBlkXp and GbndRnge. To speed up convergence in G_0W_0 calculations, the X-terminator procedure is used.[5] The final BSE calculation is performed on top of G_0W_0 band structure, and the BSEBands is converged to account for the exciton effects.

Ab initio molecular dynamics (AIMD) simulations are performed by the CP2K package[6] in the constant temperature and constant pressure (NPT) ensemble. The temperature was controlled with a conical sampling through velocity rescaling (CSVR) thermostat at room temperature (300 K), while the pressure was controlled using an isotropic cell. The time step was set to 1.0 fs. A PBE-D3 functional was used with double-zeta basis sets (DZVP-MOLOPT) and Goedecker–Teter–Hutter pseudopotentials.[7] The cut-off was set to 400 Ry. The AIMD simulations were run for approximately 5 ps to ensure equilibrium.

Electron-phonon interaction calculations are carried out by open-source code EPW v5.7,[8] the calculation of the electron and hole mobility is divided into two steps. In the first step, the phonon calculation is performed by Quantum ESPRESSO v7.1 with Standard solid-state pseudopotentials (SSSP) efficiency (version 1.3.0), automatic K points 5*5*2 are used for the scf and phonon calculation, and ecutwfc cutoff of 50 Ry and energy convergence of 10-8 Ry are set. In the second step, the Linearised Boltzmann transport

equation (BTE) is used to calculate the electron and hole mobilities, the temperature is set to 300 K and the carrier concentration is set to $1 \times 10^{13}/cm^3$.

For the input file preparation, the online QEtoolkit is used to help to prepare the SCF and NSCF files. High symmetry points along the 1st Brillouin zone is suggested by the online seekpath tool.[9] VESTA package is used to simulation the XRD patterns and display the crystal structures.[10] The effective mass of the electron and hole is fitted by the Python code Effmass[11] and the spectroscopic limited maximum efficiency (SLME) is calculated with the Python code SL3ME.[12] For the phonon dispersion spectrum, the Phonopy v.2.17.2[13] is used in conjunction with Quantum ESPRESSO v7.1, the high-symmetry path is the same to that of the electronic calculation.
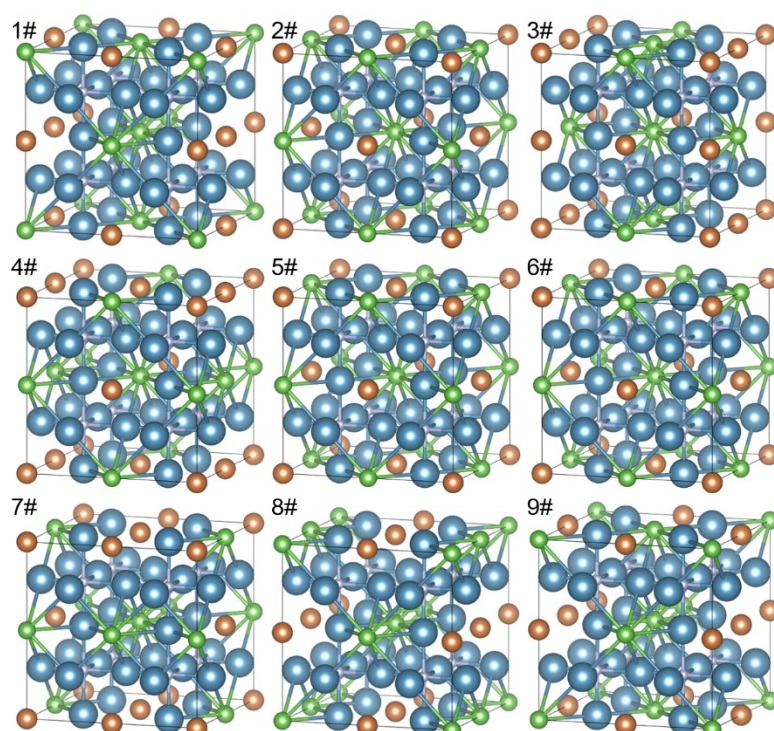

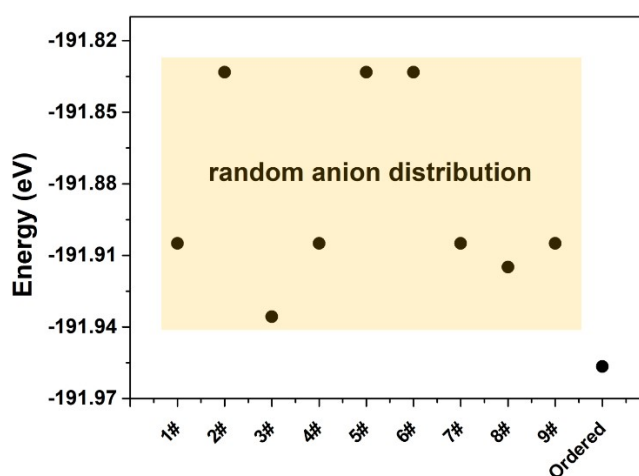Figure S1. The 9 structures with random anion distribution.

Figure S2. Total energy compassion between random anion distribution and ordered structure
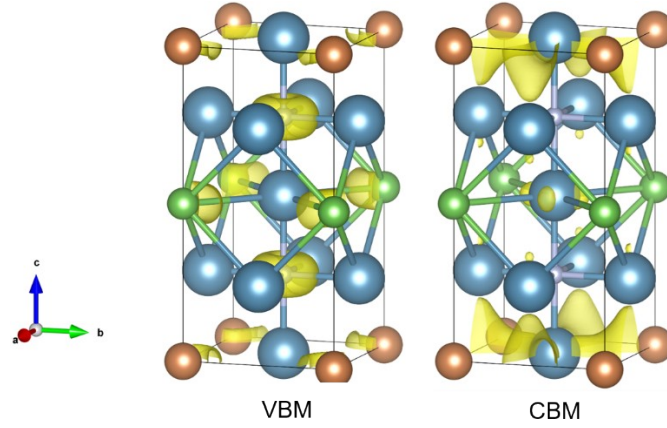
VBM   CBM

Figure S3. The charge-density isosurfaces of (a) VBM and (b) CBM states of Ca_6N_2AsSb, the isosurface level is set to 0.005.

Table S1. Effective electron and hole mass extracted from the band structure, and the electron and hole mobility calculated form electron-phonon interaction.

	m_e	m_h	μ_e (cm^2/Vs)	μ_h (cm^2/Vs)
Mean-field PBE	0.476	0.392	443.15 (xx/yy)	175.78 (xx/yy)
			56.54 (zz)	32.21 (zz)
Many-body GW	0.407	0.425		

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