

Decoding optoelectronic behavior in X_3BI_3 antiperovskite derivatives through many-body perturbation theory

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Antiperovskite derivatives have emerged as promising candidates for optoelectronic applications. However, due to the significant computational cost, their excitonic and polaronic properties remain underexplored despite being critical for optoelectronic performance. Here, we present the structural, electronic, optical, excitonic, and polaronic properties of a series of antiperovskite derivatives with the chemical formula X_3BI_3 ($X = Ca, Sr$; $B = P, As, Sb, Bi$) using state-of-the-art first-principles calculations. All the compounds exhibit direct bandgaps with $G_0W_0@PBE$ bandgap ranging from 2.42 to 3.02 eV, optimal for efficient light absorption with minimal energy loss. Exciton binding energies (0.258–0.318 eV) indicate moderate Coulomb attraction, favoring exciton dissociation. Employing the Feynman polaron model, we established the polaronic properties, where weak to intermediate carrier-phonon coupling was observed, with polaron mobilities reaching values up to $37.19 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. These properties establish X_3BI_3 materials as viable candidates for next-generation optoelectronic devices.

I. INTRODUCTION:

Halide perovskites have garnered tremendous interest in optoelectronics, due to their excellent light absorption, tunable bandgaps, and high power conversion efficiencies [1, 2]. Yet, concerns over lead toxicity and instability from volatile organic cations hinder their practical use [3, 4]. To address this, several Pb-free alternatives—such as chalcogenide perovskites, double perovskites and vacancy-ordered perovskites have been explored, though many face drawbacks like indirect bandgaps and complex synthethis. More recently, halide antiperovskite derivatives with the formula X_3BA_3 ($X = Ca, Sr$; $B = P, As, Sb, Bi$; $A = F, Cl, Br, I$) have emerged as promising, environmentally benign, and structurally robust candidates [5, 6]. Their potential has been validated by successful syntheses, highlighting their relevance for next-generation optoelectronic applications [7, 8].

Structurally, halide antiperovskite derivatives (X_3BI_3) can be viewed as an evolution from traditional perovskites (ABX_3) and antiperovskites (X_3BA). In perovskites (ABX_3), A and B are cations while X is an anion while in antiperovskites (X_3BA), the ionic roles are inverted—X becomes a cation, while B and A are anionic species [9]. Extending this framework, halide antiperovskite derivatives introduce three halide anions ($3 \times A^-$) in place of the single anion “ A^{3-} ” to satisfy charge neutrality. This structural modification not only preserves the cubic symmetry but also provides added flexibility to tune electronic and optical properties for efficient optoelectronic functionality.

Numerous studies have recently explored the potential of halide antiperovskite derivatives for optoelectronic applications, highlighting their promising electronic and optical characteristics [10–15]. For example, Sr_3PnCl_3 ($Pn = P, As, Sb$) and A_3NCl_3 ($A = Ba, Sr, Ca$) exhibit direct bandgaps in the range of 1.95–2.14 eV and 0.58–1.68 eV, alongside strong absorption and mechanical robustness, highlighting their suitability for solar energy harvesting [5, 6]. Joifullah et al. investigated the pressure-dependent structural, electronic, mechanical, and optical behavior of Sr_3PX_3 ($X = Cl, Br$), confirming their semiconducting nature and enhanced optoelectronic properties under strain [16]; however, experimental validation for these systems remains absent.

Experimental reports on iodide-based antiperovskite derivatives have further inspired the focus on these materials [7]. Several studies have explored their structural, electronic, and optical behavior [17–23]. Notably, Rahman et al. investigated Ba_3PI_3 , Ba_3AsI_3 , and Ba_3SbI_3 , reporting direct bandgaps (~ 1.9 – 2.3 eV), strong absorption, and simulated PCEs exceeding 21–29 % via SCAPS-1D, while Liu et al. assessed Ba_3MX_3 ($M = As, Sb$; $X = Cl, Br, I$), revealing direct bandgaps (1.35–1.65 eV), low effective masses, and theoretical efficiencies up to 31.9 % [24, 25]. Although these studies lay important groundwork, key optoelectronic properties—such as excitonic and polaronic response, remain unaddressed, highlighting the need for deeper theoretical insight.

To address this gap, here we present a comprehensive study of the structural, electronic, optical, excitonic, and polaronic properties of halide antiperovskite derivatives X_3BI_3 ($X = Ca, Sr$; $B = P, As, Sb, Bi$), all crystallizing

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in the cubic $\text{Pm}\bar{3}\text{m}$ phase. By employing density functional theory (DFT) [26, 27], hybrid functional (HSE06) [28], density functional perturbation theory (DFPT) [29], and many-body perturbation theory (GW-BSE) based simulations [30, 31], we explore the overall optoelectronic potential of these materials. Our calculations reveal that 5 out of 8 compositions are dynamically stable at 0 K, with $\text{G}_0\text{W}_0\text{@PBE}$ bandgaps ranging from 2.46 to 3.02 eV, falling well within the visible spectrum. Exciton binding energies obtained via the BSE formalism lie between 0.258–0.318 eV, and polaron mobility reaches values as high as $26.23 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for electrons and $37.19 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for holes, indicating promising charge transport characteristics. Computational details are provided in the Supplemental Material.

II. RESULTS AND DISCUSSIONS:

We conduct an in-depth and systematic exploration of halide antiperovskite derivatives X_3BI_3 ($\text{X} = \text{Ca}, \text{Sr}$; $\text{B} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$) to assess their suitability for optoelectronic applications. The subsequent sections provide a comprehensive evaluation of their structural and dynamical stability, followed by detailed insights into their electronic, optical, excitonic, and polaronic behavior, offering a solid theoretical foundation for guiding future experimental endeavors.

A. Crystal Structure and stability:

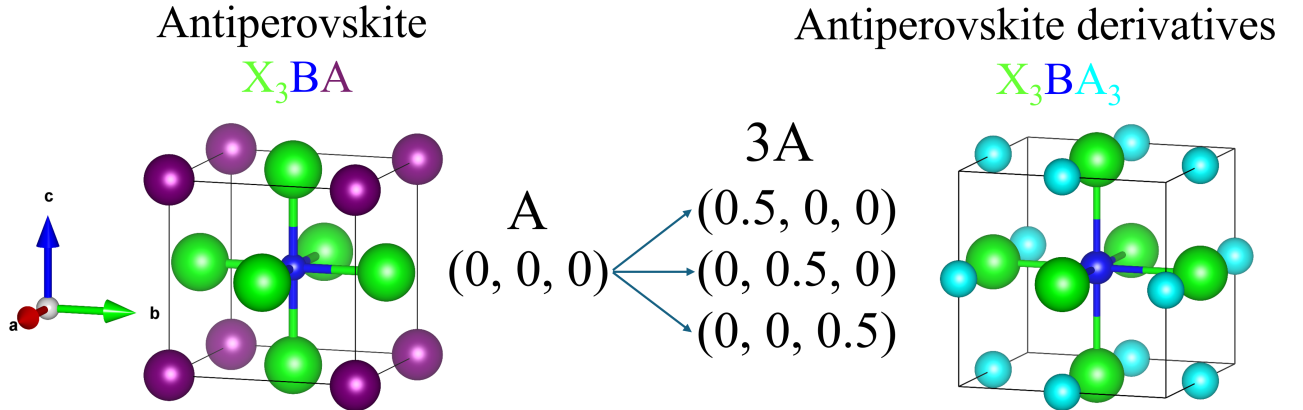


Figure 1. Schematic illustration of the transformation from antiperovskite X_3BA (left) to its derivative X_3BA_3 (right) structure. In X_3BA , the single A atom at (0, 0, 0) is replaced in X_3BA_3 by three A atoms located at (0.5, 0, 0), (0, 0.5, 0), and (0, 0, 0.5). The color scheme in the chemical formulas corresponds to the atom colors in the structures: green- X-site atoms (Ca/Sr), blue- B-site atoms (P/As/Sb/Bi), purple- “A” atom in X_3BA , and cyan- three “A” atoms in X_3BA_3 . In the present study, we specifically investigate the X_3BA_3 systems with $\text{X} = \text{Ca}, \text{Sr}$; $\text{B} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$; and $\text{A} = \text{I}$.

To examine the structural and dynamical stability of the X_3BI_3 ($\text{X} = \text{Ca}, \text{Sr}$; $\text{B} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$) compounds, we analyze their optimized crystal structures, as illustrated in Fig. 1, and assess key geometric trends in Table I. All the materials crystallize in the cubic crystal structure (space group - $\text{Pm}\bar{3}\text{m}$, No. 221) as revealed in experimental observations [7]. The unit cell contains seven atoms, with Ca/Sr at 3c (0.5, 0, 0.5), P/As/Sb/Bi at 1b (0.5, 0.5, 0.5), and I at 3d (0, 0.5, 0). A general expansion of lattice parameters and bond lengths is observed toward the heavier pnictogens (P/As/Sb/Bi), but the trend is not strictly monotonic. In Ca_3BI_3 series, the lattice constant is 6.25 Å for both Ca_3PI_3 and Ca_3AsI_3 , rising to 6.41 Å for Ca_3SbI_3 ; the X-I and X-B bond lengths increases from 3.12 Å (Ca_3PI_3) to 3.21 Å (Ca_3SbI_3) with only marginal change for Ca_3BiI_3 . The Sr_3BI_3 series follows the same overall increase ($a = 6.52 \rightarrow 6.56 \rightarrow 6.73$ Å) with Bi nearly identical to Sb, and bond lengths ($3.26 \rightarrow 3.28 \rightarrow 3.37$ Å) showing similar

small increments. At fixed B, Sr-based compounds consistently have larger lattice constants and bond lengths than Ca analogues, reflecting the larger ionic radius of Sr^{2+} .

To further validate the stability of these phases, we evaluate their phonon dispersion curves using density functional perturbation theory (DFPT) [29], as shown in Fig. 2. The absence of imaginary frequencies across the Brillouin zone confirms that Ca_3AsI_3 , Ca_3SbI_3 , Ca_3BiI_3 , Sr_3SbI_3 , and Sr_3BiI_3 are dynamically stable in the cubic phase at 0 K. In contrast, Ca_3PI_3 , Sr_3PI_3 , and Sr_3AsI_3 display negative frequencies, signaling dynamic instabilities at 0 K. These instabilities are likely associated with spontaneous symmetry breaking toward lower-symmetry distorted phases at low temperatures. However, such structures may still be stabilized at elevated temperatures, as commonly observed in many experimental cases.

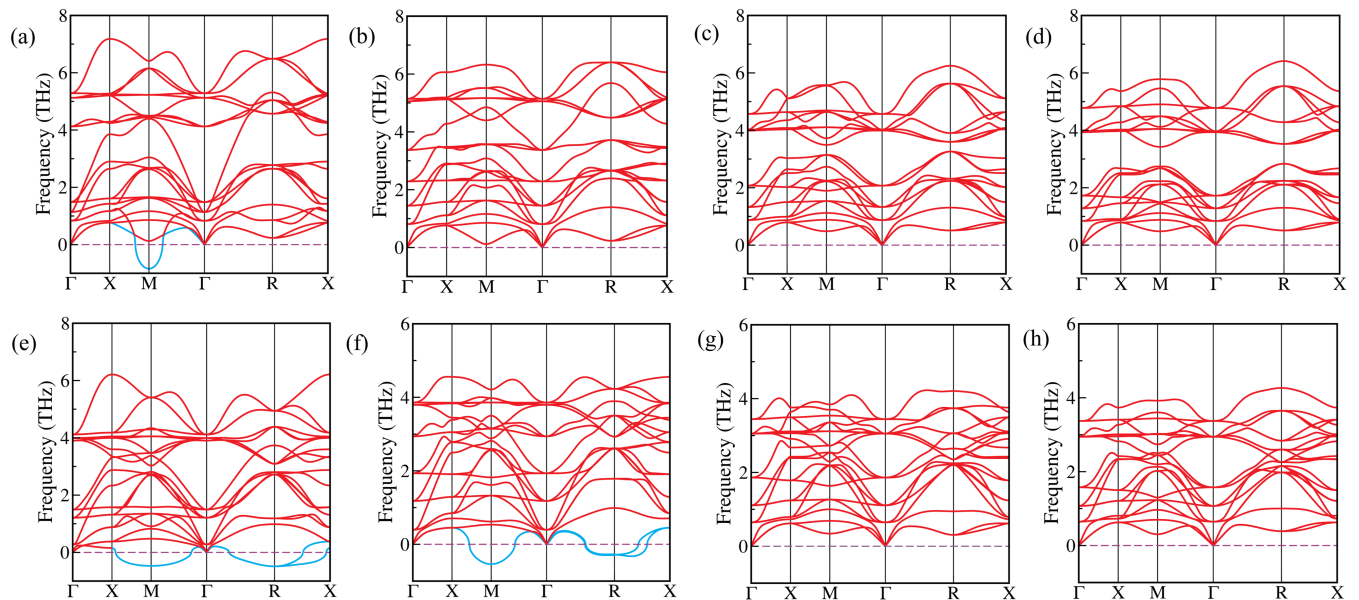


Figure 2. Phonon dispersion curves of the a) Ca_3PI_3 , b) Ca_3AsI_3 , c) Ca_3SbI_3 , d) Ca_3BiI_3 , e) Sr_3PI_3 , f) Sr_3AsI_3 , g) Sr_3SbI_3 , and h) Sr_3BiI_3 antiperovskite derivative, respectively.

To assess thermodynamic stability, the decomposition enthalpy for each X_3BI_3 compound is calculated based on the most likely binary decomposition pathways [32] (For details, see the Supplemental Material). All materials exhibit positive decomposition enthalpy values (see ΔH values in Table I), indicating energetic favorability of the X_3BI_3 phase over its binary constituents. In addition to the dynamic and thermodynamic stability, the mechanical stability and elastic properties of the systems are also studied by calculating second ordered elastic constants and all the materials are found to be mechanically stable (detailed in the Supplemental Material).

Table I. Calculated lattice parameters, bond lengths, and decomposition energies of X_3BI_3 ($\text{X} = \text{Ca}, \text{Sr}$; $\text{B} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$) antiperovskite derivatives.

Configurations	Lattice parameter ($a = b = c$)		Bond length X-I and X-B ($\text{\AA}$)	Decomposition energy ΔH (eV/atom)
	Our study ($\text{\AA}$)	Previous reports ($\text{\AA}$)		
Ca_3PI_3	6.25	6.20 [21]	3.12	0.085
Sr_3PI_3	6.52		3.26	0.140
Ca_3AsI_3	6.25	6.27 [17], 6.25 [23]	3.13	0.111
Sr_3AsI_3	6.56		3.28	0.157
Ca_3SbI_3	6.41	6.41 [33]	3.21	0.150
Sr_3SbI_3	6.73		3.37	0.185
Ca_3BiI_3	6.41	6.38 [22]	3.20	0.135
Sr_3BiI_3	6.72	6.69 [22]	3.36	0.166

B. Electronic Properties:

After confirming the structural stability, electronic structure calculations for X_3BI_3 compounds are performed, as these properties are crucial to design a photoelectric device. In this context, the partial density of states (PDOS), total density of states (TDOS), band-edge positions, and the nature of the band gap are analyzed to obtain comprehensive insights into the electronic structure.

Figure S1 illustrates the orbital-resolved density of states calculated using HSE06 xc functional for the X_3BI_3 compounds. In these systems, the valence band maximum (VBM) is primarily composed of B- p and I- p orbitals, while the conduction band minimum (CBM) is mainly composed of X-site d orbitals (Ca- $3d$ or Sr- $4d$), with minor I- p contributions, supporting p - d optical transitions. Interestingly, although Ca-containing compounds show sharper peaks near CBM, they possess wider band gaps compared to their Sr analogs. This trend can be rationalized by considering the larger lattice parameters and longer X-B and X-I bond lengths in Sr-based systems, which induce weaker orbital overlap and increased delocalization, effectively narrowing the band gap. Thus, despite sharper DOS peaks for Ca variants, the broader Sr-based lattices facilitate band edge convergence. Unlike conventional halide perovskites, here the alkaline-earth X-site cation plays a non-trivial role in shaping the CBM due to the active participation of its d orbitals.

Band structure calculations were initially performed using the PBE xc functional [34], which is known to underestimate bandgaps due to self interaction error. Therefore, to obtain more accurate bandgap estimation, we employed the HSE06 hybrid functional and the many-body perturbation theory (MBPT) based $G_0W_0@PBE$ approach [28, 35, 36]. Additionally, for the PBE calculations, spin-orbit coupling (SOC) is explicitly considered, especially due to the presence of heavy elements such as Bi, where relativistic effects significantly influence band dispersion. Notably, the PBE-SOC bandgap of Ca_3AsI_3 closely aligns with previous report [37], supporting the reliability of our calculations.

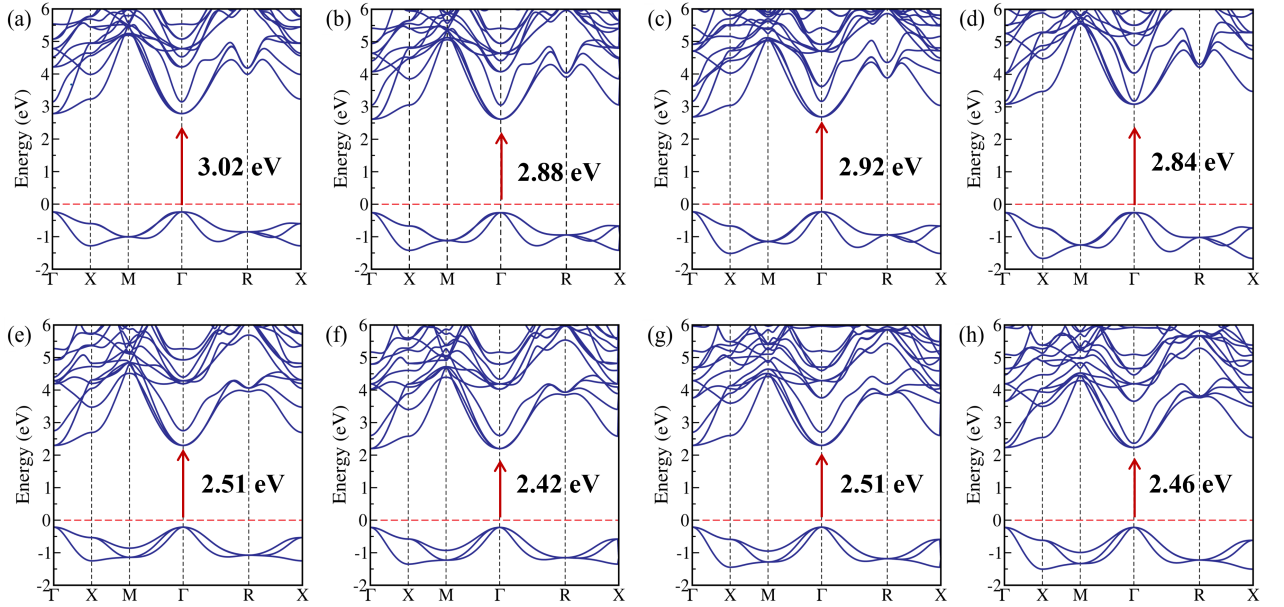


Figure 3. Electronic band structures of a) Ca_3PI_3 , b) Ca_3AsI_3 , c) Ca_3SbI_3 , d) Ca_3BiI_3 , e) Sr_3PI_3 , f) Sr_3AsI_3 , g) Sr_3SbI_3 , and h) Sr_3BiI_3 antiperovskite derivative, respectively, calculated using the $G_0W_0@PBE$ method. The fermi level is set to be zero and marked by the dashed line.

All the studied X_3BI_3 systems ($X = Ca, Sr$; $B = P, As, Sb, Bi$) exhibit direct bandgaps located at the Γ -point. The valence band maximum (VBM) and conduction band minimum (CBM) consistently occur at this high-symmetry k-point, suggesting favorable optical transitions for light absorption and emission. The bandgap values extracted from the $G_0W_0@PBE$ (Figure 3) method show a consistent trend across the series (Table II), where the bandgap decreases as we move from Ca- to Sr-based compounds for a fixed B-site atom. For instance, Ca_3PI_3 shows a G_0W_0 bandgap of 3.02 eV, while Sr_3PI_3 drops to 2.51 eV, a trend observable for the other B-site variants as well. This narrowing of

bandgap in Sr-based systems correlates with their larger lattice parameters and longer bond lengths, which can induce enhanced orbital delocalization, thereby reducing the bandgap as discussed earlier. Importantly, the direct nature of the bandgap and its alignment with the visible spectrum make these materials highly promising with minimal energy loss for optoelectronic applications such as photovoltaics and LEDs.

Table II. Computed bandgaps (E_g) of $X_3\text{BI}_3$ ($X = \text{Ca, Sr; B = P, As, Sb, Bi}$) antiperovskite derivatives using the PBE/PBE-SOC, HSE06, and G_0W_0 @PBE method. Here, m_e^* is the electron effective mass, m_h^* is the hole effective mass, and μ^* is the reduced mass of charge carriers. All values of the effective mass are in terms of free-electron mass (m_0).

Configurations	Bandgap (eV)			m_e^* (m_0)	m_h^* (m_0)	μ^* (m_0)
	PBE/PBE-SOC	HSE06	G_0W_0 @PBE			
Ca_3PI_3	1.37/1.33	2.25	3.02	0.548	0.644	0.296
Sr_3PI_3	1.27 /1.24	2.02	2.51	0.514	0.627	0.282
Ca_3AsI_3	1.33/1.23	1.40	2.88	0.541	0.572	0.278
Sr_3AsI_3	1.26/1.18	2.00	2.42	0.514	0.569	0.270
Ca_3SbI_3	1.37/1.19	2.23	2.92	0.561	0.497	0.264
Sr_3SbI_3	1.34/1.17	2.08	2.51	0.533	0.513	0.261
Ca_3BiI_3	1.28/0.82	2.09	2.84	0.557	0.444	0.247
Sr_3BiI_3	1.27/0.83	1.96	2.46	0.526	0.462	0.246

The effective masses (see Table II) are generally close to or below the free electron mass, suggesting promising transport. Notably, in Ca_3SbI_3 , Ca_3BiI_3 , Sr_3SbI_3 , and Sr_3BiI_3 , the hole masses (m_h^*) are smaller than electron masses (m_e^*), favoring hole transport. Conversely, P- and As-based compounds, having lower electron effective masses than hole masses, are expected to exhibit enhanced electron mobility and n-type transport behavior.

C. Dielectric and excitonic properties:

While the studied $X_3\text{BI}_3$ compounds demonstrate suitable bandgaps and promising electronic properties, these alone do not ensure optimal optoelectronic performance. A comprehensive understanding of their optical response and exciton formation is necessary, as these bound electron-hole states critically affect light absorption and charge transport. Fig. 4 shows the real and imaginary parts of the dielectric function, where the real part reflects material polarization and the imaginary part denotes optical absorption. All of the $X_3\text{BI}_3$ systems exhibit strong absorption beginning in the visible region ($\sim 2.1\text{--}2.7$ eV) and extending up to ~ 5 eV, covering both the visible and near-UV spectral ranges. The absorption edges display an overall red-shift trend from P to Bi, consistent with the reduction in bandgap, although small deviations occur for intermediate pnictogens.

Exciton binding energy (E_B) refers to the energy required to separate an electron-hole which plays a crucial role in optoelectronic performance. In our study, E_B is calculated using the difference between the direct quasiparticle (G_0W_0) bandgap and the first optical absorption peak from BSE calculation [38, 39]. For all $X_3\text{BI}_3$ systems, E_B ranges from 0.258 and 0.318 eV (Table III), signifying moderately bound excitons that support efficient exciton dissociation and charge transport. A-site variation (Sr vs. Ca) leads to slightly lower E_B in Ca-based systems compared to their Sr counterparts confirming their superiority in exciton dissociation.

To support and contextualize the BSE results, we additionally apply the simplified Wannier-Mott (WM) model [40, 41] to provide insight into dielectric screening and exciton delocalization (for details, see Supplemental Material). Although the WM model reproduces general trends, its oversimplified assumptions of parabolic band dispersion and isotropic screening limit its quantitative reliability, especially for systems with complex band structures. Here, to evaluate E_B , ε_{eff} must be determined first. When $E_B \gg \hbar\omega_{LO}$, as observed in our systems, the electronic contribution to the dielectric function (ε_∞) dominates the dielectric screening, making ε_∞ a valid approximation for ε_{eff} . In such cases, the influence of lattice relaxation is negligible, and the ionic contribution can be safely ignored [38, 42–44]. We employed the DFPT method [29] to estimate the ionic contribution to the dielectric function (ε_{ion}), and the electronic contribution (ε_∞) is estimated using the BSE@ G_0W_0 @PBE method. The upper (E_{Bu}) and lower (E_{Bl}) bound to the exciton binding energy is computed from the contribution of electronic dielectric constant (ε_∞) and static dielectric constant (ε_0) in place of ε_{eff} in the Wannier-Mott formula, respectively. In our study, the static dielectric constant (ε_0) is computed by the formula, $\varepsilon_0 = \varepsilon_\infty + \varepsilon_{\text{ion}}$. From Table S2, it is evident that both E_{Bu} and E_{Bl} values gradually decrease from P to Bi-containing systems, indicating stronger dielectric screening with heavier pnictogens. Notably, the E_{Bl} values are considerably lower than E_{Bu} across all systems, reflecting the dominance of electronic contribution over ionic contribution in dielectric screening.

Moreover, a comparison of E_B calculated using WM model and first-principles method reveals that GW-BSE values (0.258–0.318 eV) are consistently higher than those predicted by the WM model (0.119–0.177 eV for E_{Bu} and 3–29

meV for E_{BI}) as expected. Nevertheless, both approaches show a consistent trend of decreasing E_B from P to Bi, indicating stronger dielectric screening in heavier pnictides.

Next, using the effective dielectric constant (ε_{eff}) and the reduced mass (μ^*) of charge carriers, key excitonic parameters such as exciton radius (r_{exc}), exciton lifetime (τ_{exc}), and the probability of a wavefunction ($|\phi_n(0)|^2$) for electron-hole pair at zero separation is estimated (for details, see Supplemental Material). As seen in Table III, the exciton radius (r_{exc}) gradually increases from Ca_3PI_3 (0.88 nm) to Sr_3BiI_3 (1.15 nm), indicating more delocalized excitons in heavier pnictide systems. This increasing delocalization corresponds to decreasing $|\phi_n(0)|^2$ values implying a longer exciton lifetime in Bi-containing compounds. Such extended lifetimes may benefit optoelectronic performance by reducing carrier recombination. Overall, Sr-based systems show slightly larger excitonic radii and lower $|\phi_n(0)|^2$ than their Ca counterparts, reflecting weaker Coulomb interaction and enhanced dielectric screening. The exciton lifetime (τ_{exc}) is inversely proportional to $|\phi_n(0)|^2$ (for details, see Supplemental Material). From Table III, it is evident that $|\phi_n(0)|^2$ decreases from $0.05 \times 10^{28} \text{ m}^{-3}$ in Ca_3PI_3 to $0.02 \times 10^{28} \text{ m}^{-3}$ in Sr_3BiI_3 indicating τ_{exc} increases across the series, with heavier B-site elements (Sb, Bi) and Sr-based compounds exhibiting longer exciton lifetimes compared to their Ca counterparts. Such prolonged lifetimes are beneficial for suppressing recombination losses and improving the efficiency of optoelectronic devices.

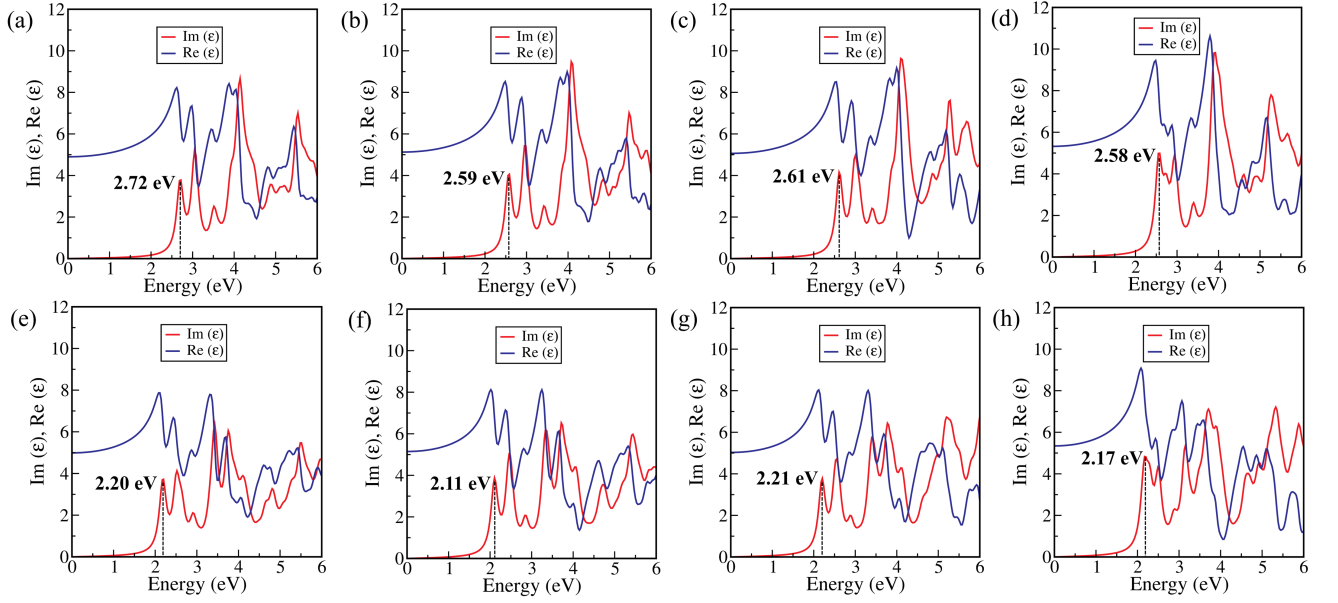


Figure 4. Real [$\text{Re}(\varepsilon)$] and imaginary [$\text{Im}(\varepsilon)$] part of the dielectric function of a) Ca_3PI_3 , b) Ca_3AsI_3 , c) Ca_3SbI_3 , d) Ca_3BiI_3 , e) Sr_3PI_3 , f) Sr_3AsI_3 , g) Sr_3SbI_3 , and h) Sr_3BiI_3 antiperovskite derivative, respectively, obtained using the BSE@ G_0W_0 @PBE method.

Furthermore, the impact of phonon screening on exciton binding energy (E_B) is determined using the correction model recently proposed by Filip et al. [45]. We determined the characteristic phonon angular frequency (ω_{LO}) using the thermal "B" scheme proposed by Hellwarth et al. [46], which involves considering the spectral average of infrared-active optical phonon modes (for details, see Supplemental Material). The correction due to phonon screening is evaluated as:

$$\Delta E_B^{ph} = -2\omega_{LO} \left(1 - \frac{\varepsilon_\infty}{\varepsilon_0} \right) \frac{\sqrt{1 + \omega_{LO}/E_B} + 3}{\left(1 + \sqrt{1 + \omega_{LO}/E_B} \right)^3} \quad (1)$$

As summarized in Table III, phonon screening leads marginal reduction in E_B , ranging from 1.97 % to 3.36 %, with the largest correction in Ca_3PI_3 and the smallest in Sr_3BiI_3 . This trend reflects slightly stronger screening effects in lighter pnictide systems, whereas heavier Bi-based compounds show weaker corrections. Overall, the reduction remains minor, indicating that electronic screening is the dominant factor influencing excitonic behavior in X_3BI_3 systems.

Table III. Calculated excitonic parameters for X_3BI_3 ($X = Ca, Sr$; $B = P, As, Sb, Bi$) antiperovskite derivatives. E_B is the exciton binding energy calculated through BSE method, r_{exc} is the exciton radius, $|\phi_n(0)|^2$ is the probability of a wavefunction for electron-hole pair at zero separation, ΔE_B^{ph} is the phonon screening corrections of exciton binding energy, and $(E + \Delta E_B^{ph})$ is the corrected values of exciton binding energy, respectively.

Configurations	E_B (eV)	r_{exc} (nm)	$ \phi_n(0) ^2$ (10^{28} m^{-3})	ΔE_B^{ph} (meV)	Reduction of E_B (%)	$(E_B + \Delta E_B^{ph})$ (meV)
Ca_3PI_3	0.305	0.88	0.05	-10.25	3.36	294.75
Sr_3PI_3	0.313	0.93	0.04	-9.01	2.88	303.99
Ca_3AsI_3	0.292	0.98	0.03	-9.57	3.28	282.43
Sr_3AsI_3	0.318	1.01	0.03	-7.05	2.22	310.95
Ca_3SbI_3	0.308	1.02	0.03	-8.73	2.83	305.17
Sr_3SbI_3	0.306	1.02	0.03	-6.40	2.09	303.91
Ca_3BiI_3	0.258	1.14	0.02	-8.07	3.13	254.87
Sr_3BiI_3	0.285	1.15	0.02	-5.62	1.97	279.38

D. Polaronic Properties:

Polaron formation originates from the interaction of charge carriers with longitudinal optical (LO) phonons, which modifies their effective transport behavior and plays a crucial role in determining the optoelectronic potential of a material. This phenomenon is quantitatively described by the Fröhlich interaction model [47, 48], which introduces a dimensionless coupling parameter α as follows:

$$\alpha = \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0} \right) \sqrt{\frac{R_\infty}{ch\omega_{LO}}} \sqrt{\frac{m^*}{m_e}} \quad (2)$$

where h is the Planck's constant, c is the speed of light, and R_∞ denotes the Rydberg's constant. Typically, $\alpha \ll 1$ reflects weak electron (or hole)-phonon coupling, while $\alpha > 10$ correspond to strong coupling [42]. The computed α values (Table IV) for the X_3BI_3 systems span a moderate range from 1.91 to 4.83, indicating intermediate electron-phonon coupling. This regime promotes delocalized large polarons, which are beneficial for maintaining charge mobility without inducing excessive localization.

To estimate the increase in carrier mass due to polaron formation, we use Feynman's extended model [49, 50]:

$$m_p = m^* \left(1 + \frac{\alpha}{6} + \frac{\alpha^2}{40} + \dots \right) \quad (3)$$

The calculated mass enhancements range from 1.47 to 2.39 for electrons and 1.41 to 2.11 for holes with the largest increase observed in Ca_3PI_3 due to its stronger coupling. A general trend is observed where polaron mass decreases from lighter (P) to heavier (Bi) pnictogens, which aligns with the weakening of α .

It is important to note that polaron formation can lead to a reduction in the energies of electron and hole quasi-particles (QPs). This energy lowering, referred to as the polaron energy (E_p), can be evaluated from the coupling constant α using the following relation [51, 52]:

$$E_p = (-\alpha - 0.0123\alpha^2)\hbar\omega_{LO} \quad (4)$$

For Ca_3PI_3 , Sr_3PI_3 , Ca_3AsI_3 , Sr_3AsI_3 , Ca_3SbI_3 , Sr_3SbI_3 , Ca_3BiI_3 , and Sr_3BiI_3 , the QP gap is reduced by 117.75, 98.49, 89.61, 75.26, 77.59, 65.27, 62.44, and 52.69 meV, respectively. Comparing these values with E_B from Table III, we conclude that the charge-separated polaronic states are less stable than the bound excitons [38]. Next, we calculated polaron mobilities (μ_p) for electrons and holes using the Hellwarth variational model [46]:

$$\mu_p = \frac{(3\sqrt{\pi}e)}{2\pi c\omega_{LO}m^*\alpha} \frac{\sinh(\beta/2)}{\beta^{5/2}} \frac{w^3}{v^3} \frac{1}{K(a, b)} \quad (5)$$

with

$$K(a, b) = \int_0^\infty du [u^2 + a^2 - b \cos(vu)]^{-3/2} \cos(u) \quad (6)$$

Here, a^2 and b are determined as:

$$a^2 = (\beta/2)^2 + \frac{(v^2 - w^2)}{w^2 v} \beta \coth(\beta v/2) \quad (7)$$

$$b = \frac{v^2 - w^2}{w^2 v} \frac{\beta}{\sinh(\beta v/2)} \quad (8)$$

where $\beta = \hbar c \omega_{LO} / k_B T$, w and v are temperature-dependent parameters (for details, see Supplemental Material). Polaron mobility values depicted in Table IV lie between 7.23–37.19 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, with Sr_3BiI_3 exhibiting the highest μ_p for electrons (26.23 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) and Ca_3BiI_3 exhibiting highest μ_p for holes (37.19 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$). We also observe an increasing trend in μ_p from P to Bi, attributed to reduced α and m_p . Compared to MAPbI_3 , an well-known halide perovskite, our systems exhibit lower mobilities [53], yet remain competitive for optoelectronic use, particularly where thermal stability and non-toxicity are prioritized. Overall, Bi-based systems show improved mobility due to lower polaron mass and weaker coupling, underscoring their promise for efficient charge transport in lead-free photovoltaic applications.

Table IV. Polaron parameters corresponding to electrons (e) and holes (h) for X_3BI_3 ($\text{X} = \text{Ca}, \text{Sr}; \text{B} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$) antiperovskite derivatives.

Configurations	ω_{LO} (THz)	α		m_p/m^*		E_p (meV)		μ_p ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	
		e	h	e	h	e	h	e	h
Ca_3PI_3	3.00	4.45	4.83	2.24	2.39	56.37	61.38	9.84	7.23
Sr_3PI_3	2.79	3.72	4.11	1.97	2.11	46.69	51.80	14.90	10.39
Ca_3AsI_3	3.52	2.84	2.93	1.68	1.70	44.16	45.45	18.59	16.79
Sr_3AsI_3	2.72	3.20	3.37	1.79	1.85	36.64	38.62	19.07	15.95
Ca_3SbI_3	3.94	2.43	2.29	1.51	1.55	37.59	40	21.19	26.03
Sr_3SbI_3	2.91	2.67	2.62	1.62	1.61	33.07	32.42	22.95	24.48
Ca_3BiI_3	3.91	2.14	1.91	1.47	1.41	35.15	31.29	25.50	37.19
Sr_3BiI_3	2.75	2.50	2.34	1.57	1.53	28.29	26.46	26.23	32.65

III. CONCLUSIONS:

In summary, our systematic investigation of the structural, electronic, excitonic, and polaronic properties of X_3BI_3 ($\text{X} = \text{Ca}, \text{Sr}; \text{B} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$) systems using state-of-the-art first-principles calculations unveils, all compounds are structurally and mechanically stable. Dynamical stability was confirmed for five out of eight systems at 0 K through phonon calculations based on DFPT. These materials exhibit direct $\text{G}_0\text{W}_0\text{@PBE}$ bandgaps ranging from 2.42 to 3.02 eV, ideal for efficient light-harvesting with minimal energy loss. Exciton binding energy ranges between 0.258 and 0.318 eV, ensuring efficient exciton dissociation. A combined analysis using the BSE and Wannier-Mott models confirms the dominant role of electronic screening, with phonon screening contributing marginal corrections (1.97–3.36%) in E_B . Fröhlich coupling constants ($\alpha = 2.14\text{--}4.83$) indicate weak-to-intermediate electron-phonon interaction, facilitating large polaron formation. This is further supported by moderate polaron masses and polaron energies. Notably, the polaron mobilities reach up to 37.19 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, highlighting the potential of these materials for efficient charge transport. Taken together, our findings suggest that X_3BI_3 compounds offer a promising platform for lead-free, stable, and efficient optoelectronic applications.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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