First principles calculations of the optoelectronic properties of magnesium substitutes in Lead based ABX₃ compounds

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Abstract. Perovskites are potential materials for the fabrication of cheap and efficient solar cells with a suitable Electron Transport Layer (ETL) as base. Currently, the most efficient Perovskite Solar Cells (PSCs) are made of Methyl Ammonium Lead Iodide (MALI), CH₃NH₃PbI₃, typically with anatase ETL, which is toxic due to the presence of lead. Magnesium is a non-toxic potential substitute for lead in MALI PSCs. This study focuses on simulating and calculating the optoelectronic properties of magnesium based perovskites and comparing them with those of the lead-based perovskites, to know if they will serve as a better substitute for lead (due to its high toxicity). We performed atomistic simulations of Methyl Ammonium Magnesium Iodide (MAMI), CH₃NH₂MgI₃ and Methyl Ammonium Lead Iodide (MALI), CH₃NH₃PbI₃, both in the triclinic and orthorhombic phases, using Density Functional Theory within the Generalised Gradient Approximation using Ultra Soft Perdew-Burke-Enzerhof of pseudopotentials. All atomistic simulations were done using well-converged k-points and cut-off energies. Results obtained showed that both MAMI and MALI possess similar optoelectronic properties in the triclinic and orthorhombic phases, strongly indicating that MAMI based perovskite materials are potential replacement candidates for fabricating cheap and efficient solar cells with little or no toxicity.

1. Introduction
The emergence of the environmentally-benign [1], cheap-to-produce [2], and quick-evolving efficient perovskite solar cells (PSCs) [3] has been ground-breaking in the production of renewable energy from solar energy [4]. PSCs are made of organic and hybrid (organic-inorganic) materials [5], and classified as third generation solar cells [6], coming after photovoltaic (PV) solar cells based on thin film cells (second generation) and PV solar cells based on single crystalline and multijunction cells (first generation) [7]. Perovskites generally have the formula ABX₃ [8], where A (an organic or inorganic ion) and B (a metal ion) are cations and X (a halide) is an anion [9]. The highest Power Conversion Efficiency (PCE) of PSCs achieved currently, is 22% [10] and there is indeed still room for improvement. Most times, the metal ion used in the perovskite material is lead (Pb²⁺) [11], coupled with methylammonium ion (CH₃NH₃⁺) [12] and a halide. Due to their interesting optoelectronic properties, perovskites can function both as light harvesters (absorber material) and as a hole transport material (HTM) [13]. However, owing to the toxicity level due to the presence of lead, there is a need to find a substitute metal with little or no toxicity, yet possessing optoelectronic properties good enough to compete with the PCE level attained by the lead-based PSCs. Such optoelectronic properties include optimum bandgap for absorption of photons in the visible range, direct band gap [14], low electron and hole effective masses [15], low exciton binding energy, and long carrier lifetimes. Several theoretical and experimental attempts have been made to totally or partially replace lead, however, as at now, none of these attempts has led to the discovery of non-toxic, lead-free and stable perovskites that have similar optoelectronic properties to lead-based perovskites. Previous studies include the total replacement of Pb²⁺ with Sn²⁺ [16]; the partial replacement of Pb²⁺ with Ge²⁺ [17] [18]; Ca²⁺; Sr²⁺; Cd²⁺; and Bi, to mention a few. MgI₂ which crystallizes into the P-3m1 crystal group [19], similar to that of PbI₂, suggests that Mg, a non-toxic and widely available metal, is a...
potential replacement for Pb. This study was designed to calculate the optoelectronic properties of magnesium substitutes in lead based ABX$_3$ compounds.

**2. Methods**

Atomistic simulations based on Density Functional Theory (DFT) [20] were performed using ultra-soft Perdew-Burke-Ernzerhof (PBE) [21] pseudopotentials [22] within the Generalized Gradient Approximation [23] for six different structures: triclinic-MALI, orthorhombic-MALI, alpha-MAMI, beta-MAMI, di-MAMI and orthorhombic-MAMI using Quantum Espresso (QE) [24]. All simulations were carried out as follows:

1. Convergence tests for automatically generated Monkhorst-Pack K-point scheme [25] and Kinetic cutoff energy were carried out for all the structures to determine the optimum simulation parameters.

2. Structure optimization (or geometry optimization) was carried out for the six different structures to obtain the ground state energy (minimum force) suitable for QE to predict the ground state properties (such as; bandgaps, effective mass of electron and hole, band structure and density of states) of these systems.

3. After all the different optimizations were achieved, the bandgaps for the different fully optimized structures were calculated by running a Self-Consistent Field (SCF) calculation. The symmetry was set to high in the input file, and smearing was also included, to obtain the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) in the output results.

4. The Density of States (DOS) and the Partial Density of States (PDOS) for the different structures were calculated by using a denser grid of K-points: 24x24x24 for the triclinic alpha-MAMI, beta-MAMI, and triclinic-MALI, 4x4x4 for the remaining perovskite structures to show the contribution of each atomic orbital (number of states) at each energy level.

5. The electron and hole effective masses were calculated for all the six different structures.

6. The conductivity effective density of states and the effective density of states in the valence bands were also calculated at a temperature of 300K, using the results obtained from hole and electron effective masses.

7. Phonon calculation at the gamma point was carried out to achieve the dielectric constant for the different structures. This is an important parameter in determining the PCE of the systems.
3. Results
3.1 Convergence Tests
The kinetic cutoff energy for all structures converged at 35 Ry. The recommended optimum kinetic cutoff energy for ultrasoft pseudopotentials is between 30 and 40 Ry. These low kinetic cutoff energies reduce the number of plane waves needed to run the subsequent simulations itemized in the methods. Higher kinetic energy cutoffs allow for more plane waves and in turn increase the time to complete simulations. It is therefore advisable to use pseudopotentials that converge for low kinetic cutoff energies, in order to efficiently maximize computational resources. The charge density cutoff was 350 Ry for all systems, as the charge density cutoff for ultrasoft pseudopotentials is 8-12 times the kinetic cutoff energy.

The k-points for all structures converged at 4x4x4. The converged k-points were centred on the gamma point. In contrast to kinetic cutoff energy convergence tests, k-points convergence tests do not exhibit a monotonous descent in total energy as k-points increase [26]. The converged k-points indicates the minimum k-point grid required to run simulations, as a result the converged k-points or a larger grid can be used for subsequent simulations itemized in the methods. The higher the k-points, the more accurate the electronic structure calculations [27].

3.2 Structure Optimisation
The optimized triclinic-MALI, alpha-MAMI, beta-MAMI and Di-MAMI structures are triclinic. The optimized orthorhombic-MALI and orthorhombic-MAMI structures are orthorhombic. Each structure was optimised using fixed and/or variable cell relaxations in order to obtain optimum atomic coordinates and cell parameters for each system. For the triclinic-MALI, alpha-MAMI, beta-MAMI and di-MAMI, fixed cell relaxations were run first, and subsequently variable cell relaxations. For the orthorhombic-MALI and orthorhombic-MAMI, only variable cell relaxations were run.

The fixed cell relaxations of triclinic-MALI, alpha-MAMI, beta-MAMI and di-MAMI, had the resultant forces of 0.041 eV/A, 0.350 eV/A, 0.066 eV/A and 0.204 eV/A respectively. From these forces, it is clear that the triclinic-MALI and beta-MAMI structures achieved better results in terms of the minimisation of forces after the fixed cell relaxation. It is important to note that triclinic-MALI, alpha-MAMI and beta-MAMI all have 12 atoms in the unit cell, while di-MAMI, orthorhombic-MALI and orthorhombic-MAMI have 24, 48 and 48 atoms respectively.
Also show that MAMI and MALI in the orthorhombic phases have the same lattice cell in the result of optimization have being with the trend for pre er for both systems are the same, as well as a slight di ly. Not all structures exhibited indirect band gaps, the calculated indirect band gap. From the results of the structural optimization calculations, it was varied with increase in k points. These results a result of the relaxations show that the most optimized MAMI structure is in the orthorhombic phase.

From Table 1, the calculated direct band gaps for triclinic MALI, orthorhombic MALI, alpha-MAMI, beta-MAMI, di-MAMI and orthorhombic-MAMI, are 1.63 eV, 1.78 eV, 1.73 eV, 1.73 eV, 1.50 eV and 1.47 eV respectively. Not all structures exhibited indirect band gaps, the calculated indirect band gaps for triclinic MALI, alpha-MAMI, beta-MAMI are 1.58 eV, 1.41 eV, 1.36 eV respectively. Both MALI and MAMI exhibit direct and indirect band gaps in the triclinic phase, while in the orthorhombic phase they only exhibit direct band gaps. Despite the fact that alpha-MAMI and beta-MAMI have the same number of atoms, atom type and crystal phase, yet the indirect band gap values differ. This shows that there is an effect of atomic positions and configuration on the optoelectronic properties of a material, in particular the band gap. Triclinic-MALI exhibited instability in the value for the indirect band gap. The value of the indirect band gap for triclinic-MALI was unstable as it varied with increase in k-points. This was not the case for MAMI in the triclinic phase, which exhibited a stable indirect band gap. From the results of the structural optimization calculations, it was
deduced that MAMI in the orthorhombic phase is the most optimized MAMI structure. The band gap of MAMI in the orthorhombic phase is 1.47 eV while that of MALI is 1.78 eV, indicating that MAMI in the orthorhombic phase is a better candidate for light absorption compared to MALI.

3.4 Total and Partial Density of States
From Fig 2 the focused total and partial density of states for triclinic-MALI and orthorhombic-MALI show that the I 5Pₓ, 5Pᵧ, 5Pₜ are the major contributors to the HOMO of triclinic-MALI and orthorhombic-MALI, while a minimum contribution from Pb 6S is also observed for both structures. The contributions of I 5Pₓ, 5Pᵧ, 5Pₜ are of similar magnitude. The Pb 6Pₓ, 6Pᵧ and 6Pₜ are the major contributors to the LUMO of triclinic-MALI and orthorhombic-MALI, howbeit these contributions even though major, are low in magnitude.

The focused total and partial density of states for alpha-MAMI and beta-MAMI show that the I 5Pₓ, 5Pᵧ, 5Pₜ are the major contributors to the HOMO of alpha-MAMI and beta-MAMI, while a minimum contribution from N 1S is also observed for both structures. The contributions of I 5Pₓ, 5Pᵧ, 5Pₜ are of similar magnitude for beta-MAMI, while I 5Pₓ has the highest contribution for beta-MAMI. The Mg 2Pₓ, 2Pᵧ, 2Pₜ and H 1S are the major contributors to the LUMO of alpha-MALI and beta-MALI. In contrast to triclinic-MALI and orthorhombic-MALI, these contributions are higher in magnitude. For alpha-MAMI, all the Mg 2P orbitals had similar magnitudes of contribution, while that of H 1S was slightly higher. For beta-MAMI the Mg 2Pₓ and 2Pᵧ had similar magnitude of contribution while the Mg 2Pₜ had the highest magnitude of contribution.

The focused total and partial density of states for di-MALI and orthorhombic-MALI shows that the I 5Pₓ, 5Pᵧ, 5Pₜ are the major contributors to the HOMO of di-MALI and orthorhombic-MALI, while a minimum contribution from N 1S is also observed for both structures.

The contributions of I 5Pₓ, 5Pᵧ, 5Pₜ are of similar magnitude for both structures. The Mg 2Pₓ, 2Pᵧ, 2Pₜ and H 1S are the major contributors to the LUMO of di-MALI and orthorhombic-MALI, in contrast to triclinic-MALI and orthorhombic-MALI, these contributions are higher in magnitude. All the Mg 2P orbitals had similar magnitudes of contribution while that of H 1S was slightly higher. The total and partial density of states plots show that both MALI and MAMI have similarly corresponding orbitals contributing to the HOMO and LUMO energy levels, with varying magnitudes of contribution.

3.5 Band Structure, Effective Mass and Effective Density of States
The direct band gaps, indirect band gaps and fermi levels can be viewed from the plots (FIG 3). It is important to note that for all plots the fermi level has been set at 0 eV. The fermi level for triclinic-MALI is closer to the conduction band, indicating that it is an n-type material. The fermi level for orthorhombic-MALI is closer to the valence band, indicating that it is a p-type material. The fermi level for the for alpha-MALI is halfway between the conduction band and the valence band, indicating that alpha-MALI is neither n-type or p-type.

The fermi level for beta-MALI is slightly above the halfway mark between the conduction and valence band, closer to the conduction band than the valence band, indicating that beta-MALI is an n-type material. The fermi level of di-MALI is closer to the conduction band than the valence band. The fermi level for orthorhombic-MALI is closer to the valence band than the conduction band, indicating it is a p-type material. The calculated electron conductivity effective masses for triclinic-MALI, orthorhombic-MALI, alpha-MALI, di-MALI and orthorhombic-MALI are 0.02 mₓ, 0.03 mᵧ, 0.02 mₜ, 0.03 mₓ, 0.03 mᵧ and 0.03 mₜ, respectively. The calculated electron density of states effective masses for triclinic-MALI, orthorhombic-MALI, alpha-MALI, di-MALI and orthorhombic-MALI are 0.02 mₓ, 0.05 mᵧ, 0.02 mₜ, 0.03 mₓ, 0.03 mᵧ and 0.03 mₜ, respectively. The calculated hole density of states effective masses for triclinic-MALI, orthorhombic-MALI, alpha-MALI, di-MALI and orthorhombic-MALI are 0.04 mₓ,
0.03 \text{m}_h, 0.02 \text{m}_h, 0.11 \text{m}_h, \text{and} 0.20 \text{m}_h \text{respectively. The calculated CB effective density of states for triclinic-MALI, orthorhombic-MALI, alpha-MAMI, \text{di-MAMI} \text{and or} \text{thorhombic-MAMI} \text{are} 9.33 \times 10^{16} \text{cm}^3, 3.23 \times 10^{17} \text{cm}^3, \quad 4.91 \times 10^{16} \text{cm}^3, \quad 1.35 \times 10^{17} \text{cm}^3 \text{and} \quad 1.46 \times 10^{17} \text{cm}^3 \text{respectively. The calculated VB effective density of states for triclinic-MALI, orthorhombic-MALI, alpha-MAMI, \text{di-MAMI} \text{and or} \text{thorhombic-MAMI} \text{are} 2.35 \times 10^{17} \text{cm}^3, \quad 1.42 \times 10^{17} \text{cm}^3, \quad 6.38 \times 10^{16} \text{cm}^3, \quad 9.18 \times 10^{17} \text{cm}^3 \text{and} \quad 2.22 \times 10^{18} \text{cm}^3 \text{respectively. The effective density of states indicate the density of charge carriers close to the conduction and valance bands respectively. This is an important result as it helps to know the number of charge carriers to expect in the respective PSCs. The effective density of states for the conduction and valence bands are of the same order of magnitude for MAMI and MALI in the triclinic and orthorhombic phases, with the exception of the valence band effective density of states of di-MAMI and orthorhombic-MAMI due to the relatively high values obtained for their respective hole density of states effective mass.}

FIG. 2. a) Focused density of states plot for optimised triclinic-MALI structure. b) Focused density of states plot for optimised orthorhombic-MALI structure. c) Focused density of states plot for optimised alpha-MAMI structure. d) Focused density of states plot for optimised beta-MAMI structure. e) Focused density of states plot for optimised di-MAMI structure. f) Focused density of states plot for optimised orthorhombic-MAMI structure.
3.6 Dielectric Constant
From Table 1, the calculated dielectric constants for triclinic-MALI, orthorhombic-MALI, alphaMAMI, beta-MAMI, di-MAMI and orthorhombic-MAMI are 6.66, 5.30, 3.55, 3.54, 3.58 and 4.11 respectively. The dielectric constants for MALI are higher that those for MAMI. These values were extracted from the results of the phonon calculation of the respective systems at the gamma point. From these values, it is clear that the configuration of atoms has an effect on the dielectric constants MALI and MAMI, as their respective dielectric constants vary from phase to phase.

![Graphs](image-url)

FIG. 3. a) Band structure plot for optimised triclinic-MALI structure. b) Band structure plot for optimised alpha-MAMI structure. c) Band structure plot for optimised di-MAMI structure. d) Band structure plot for optimised orthorhombic-MALI structure. e) Band structure plot for optimised beta-MAMI structure. f) Band structure plot for optimised orthorhombic-MAMI structure
4. Conclusion
This study focused on calculating the optoelectronic properties of magnesium substitutes in lead based ABX$_3$ compounds, and comparing them with those of the lead based ABX$_3$ compounds. From the structural investigation, the most observed optimized MALI and MAMI perovskite structures are orthorhombic-MALI and orthorhombic-MAMI. Results obtained showed that both MAMI and MALI possess similar optoelectronic properties in the triclinic and orthorhombic phases and strongly indicating that MAMI based perovskite materials are potential replacement candidates for fabricating cheap and efficient solar cells with little or no toxicity.

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