MECHANICAL STABILITY STUDY OF BULK FAXM₃ PEROVSKITES

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Abstract— We investigate the mechanical stability (MS) of Formamidinium (FAXM₃) based perovskite structures using first-principles density functional theory calculations with Van der Waals interactions (DFT+vdW). The organic cation and its interaction with the inorganic species play a crucial role in determining the MS of the whole structure. We obtained an orthorhombic structure for all the calculations generated from the Pm3m space group. The elastic constant (EC) values considering all the nine independent deformations paths needed to define the MS. We noticed that both the cation and the hydrogen (H) to halogen (iodide, bromide, and chloride) charge distributions (CD) influence the EC results. The Mulliken-charge results clearly demonstrate the bonding interactions between the cation and the inorganic species.

Keywords— *formamidinium, perovskites, elastic constant, mechanical stability*.

I. INTRODUCTION

Recent days, the formamidinium (FA) based (FAXM₃) perovskites are the most noticeable absorber layer for organic-inorganic perovskites based photovoltaic (PV) applications, where X is a lead (Pb) or tin (Sn), and M is a halogen such as an iodide (I), bromide (Br), chloride (Cl). The power conversion efficiency (PCE) of the perovskite solar cells (PSc) is presently lifting to 25% due to the smaller bandgap with a broader absorption range, larger organic cation radii, long diffusion length, low exciton binding energy, both higher thermal stability, and phonon relaxation lifetime. [1-7] Despite these advantages, the black colored alpha-phase FA perovskite is not stable at room temperature, and the stable yellow-colored delta-phase is not suitable for the PV field. [8] Recently published experimental reports prove that the incorporation of an inorganic cation such as cesium, or mixed halides (I, Br, and Cl) helps to restrict the phase transition from alpha to the delta. [9-11] Also, some research papers report that the theoretical analysis, based on the FA cation to understand the mechanism behind the phase transformation. [3, 12-15] J. F. Wang *et al.* found that the orientation of the FA cation and the Van der Waals (vdW) interaction between the cation to the inorganic subcell influence the structural behavior. [12] E. D. Indari *et al.* findings demonstrate that the formamidinium lead iodide (FAPbI₃) perovskites display the lower density of states (DOS) compared to the methylammonium lead iodide (MAPbI₃) perovskites. [13]

D. Li *et al.* results were showing that the overlap integral charge density of MAPbI₃ perovskites is higher than the FAPbI₃. [3] S. Kanno *et al.* found that the organic FA cation freely rotates the N-N bond axis compared to the C-N bond axis. [14] Recently, L. Geo *et al.* studied the mechanical properties over the FA perovskite structure, and they found that the planar FA cation interaction with different halides significantly affects the structural and mechanical properties of the perovskites. [15] Still, there is a lot of research investigations that need to understand the complete mechanism behind the perovskites and its natural behavior.

Therefore, in this work, we thoroughly analyze the mechanical stability of six different FA organic cation-based perovskite conventional models such as FAPbI₃, FAPbBr₃, FAPbCl₃, FASnI₃, FASnBr₃, and FASnCl₃ from elastic-constant results using the first-principles density functional theory (DFT) calculations with van der Waals interactions. Our results show that the X and M site substitution over the FA cation perovskite positively affect the structural properties. The obtained Mulliken-charge analysis and elastic-constant results are helping to understand the different behavior of FA cation-based perovskite models.

II. COMPUTATIONAL DETAILS

We constructed the FA-based unit-cell model based on previous reports. The initial lattice parameter and the reduced coordinates for every atom, as well as the space group (Pm3m), were taken from a previously published result. [6] We replaced the Sn instead of Pb for all the Sn-based models. DFT-vdW scheme, by the Tkatchenko-Scheffler (TS) dispersion model [16], through the CASTEP module [17] available in the Material studio package [18] was used for all the calculations. The generalized gradient approximation to the exchange-correlation functional Perdew-Burke-Ernzerhof (GGA−PBE) [19] was considered, with ultra-soft pseudopotentials [20]. A k-point mesh of 4×4×4 for all the conventional unit cell models (32 points and a 0.035 separation) together with a plane wave cutoff energy of 400 eV were chosen, by carefully testing the convergence after a full relaxation under the BFGS algorithm [21]. The tolerance criteria of force, stress, and displacement are equal to 0.0300 eV/Å, 0.05 GPa, and 0.001 Å.
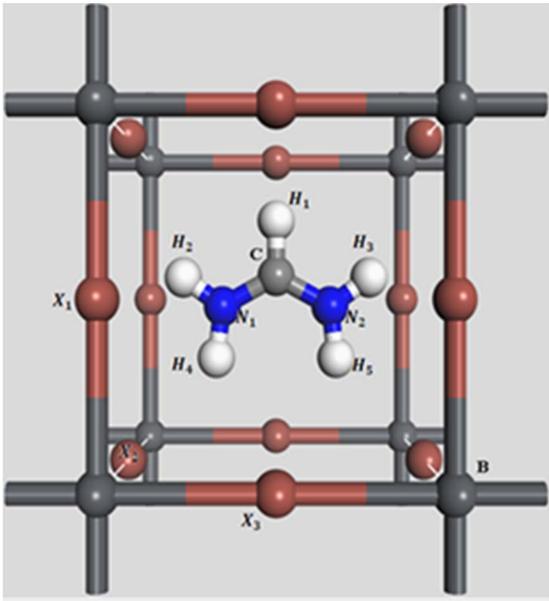
Fig. 1. FAXM$_3$ cubic representation. Where B is lead (Pb) or tin (Sn); X$_1$ is I$_1$, Cl$_1$, Br$_1$; X$_2$ is I$_2$, Cl$_2$, Br$_2$, and X$_3$ is I$_3$, Cl$_3$, Br$_3$.

III. RESULTS AND DISCUSSIONS

The calculated lattice parameters value, b/a and c/a ratios, volume, and the ground state energy for the six different FA based perovskite models (FAPbI$_3$, FAPbBr$_3$, FAPbCl$_3$, FASnI$_3$, FASnBr$_3$, and FASnCl$_3$) shown in Fig. 2. For all the calculations we initiate with the same lattice parameter (a= 6.36 Å [6]), and all the six unit-cell models, we ended with an orthorhombic structure. In general, nine independent strain patterns are needed to determine each adiabatic EC values for an orthorhombic structure. [22, 23]. The obtained lattice parameter values of the conventional FAPbI$_3$ model (a= 6.47, b=6.30, c=6.41 Å) is consistent with the previous results. [14, 15] After substituting the different halides such as Br and Cl instead of I into the same structure, the lattice parameters were significantly reduced. (see Fig.2) We also tested with the Sn as a replacement for Pb in the same configured model. Interestingly, the lattice parameter values for the FASnI$_3$ structure (a= 6.40, b=6.19, c=6.30 Å) is significantly diminished than Pb based models due to the size of the Sn compared to Pb. At the same time, we are placing the various halides instead of I in the Sn-based models, which also follows the tendency like Pb-based unit cell models. As a result, the lattice parameter values (a, b, c) for both lead and tin-based perovskites decreasing in the following order, I, Br, and Cl, respectively (see Fig.2). Due to the halide size (Br, and Cl smaller than I), it influences the bond angle as well as the bond length (i.e., Pb (Sn) - X (I, Br, Cl) – Pb (Sn)), which is effectively distorted the perovskite structure [15]. The obtained lattice parameter values agree with L. Geo *et al.* reported results for Sn and lead-based perovskites (a= 6.67, b=6.50, c=6.61 for FAPbI$_3$, a=6.30, b=6.08, c=6.21 for FAPbBr$_3$, a=6.62, b=6.46, c=6.53 for FASnI$_3$ and a=6.26, b=6.03, c=6.14 for FASnBr$_3$), respectively. [15] The values of b/a and c/a ratios confirm that the I based conventional model (FAPbI$_3$) shows the closest cubic range (pseudo-cubic) value compared to other Pb and Sn-based unit-cell models. The calculated ground state energy, as well as the unit-cell volume values, are shown in Fig. 2. The obtained ground state energy is entirely different for Pb and Sn-based

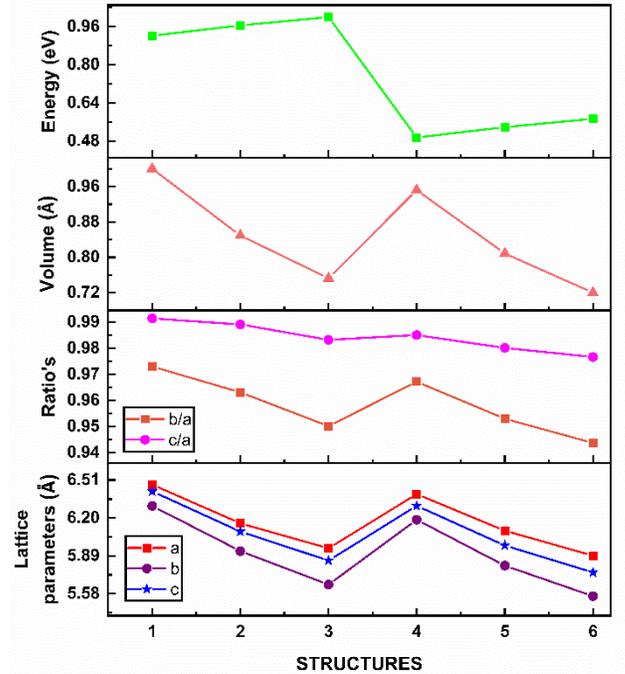perovskites due to the X (either Pb and Sn) site interaction to halogens.

Fig. 2. Results of lattice parameters (a, b, c), volume, and ground-state energy for optimized FAMX$_3$ structures. In X-axis 1, 2, 3, 4, 5 and 6 belongs to FAPbI$_3$, FAPbBr$_3$, FAPbCl$_3$, FASnI$_3$, FASnBr$_3$, FASnCl$_3$, respectively.

The obtained Mulliken-charge analysis shows that the charge populations and the bond length in between the halogen (I, Br, and Cl) to the FA cation, which influences both the structural and the mechanical stability behavior of all the six conventional models. (see table. I) Typically, the halogen, which is placed in the perpendicular to the plane of the molecule contribution is higher than the other ones. Both the halogen and X site substitution gives the different charge distribution to the FA organic cation to the inorganic sub-cells. From table. I, it is easily understandable that hydrogen to halogen (I, Br, and Cl) bonding, as well as the charge distribution, is crucial to understand the structural behavior, especially H$_4$ and H$_5$ to specific halogen position (i.e., I$_2$, Br$_2$, and Cl$_2$) decides the structural response. I and Br based models (both Pb and Sn) having the highest bond population value, which belongs to H$_4$ and H$_5$ to I$_2$ or Br$_2$ bonds. At the same time, H$_2$ - Cl$_2$ and H$_3$ - Cl$_2$ bonding demonstrate a little higher bond population than H$_4$ - Cl$_2$ and H$_5$ - Cl$_2$ bonding for both Cl based lead and tin models. We noticed that no bonding contribution occurred in between I to either Pb or Sn in the FAPbI$_3$ and FASnI$_3$ models compared to Br and Cl-based conventional models. (see table. I) Surprisingly, Cl contained models confirm that all three Cl position (Cl$_1$, Cl$_2$, and Cl$_3$) interact with lead or tin, especially to the Pb$_1$ or Sn$_1$ atom. The contribution occurred in between Br$_1$-Pb$_1$, for the Br-based Pb-model, and Br$_1$-Pb$_1$ & Br$_2$-Pb$_1$ bonding for the Sn-based model, which is entirely different from the I and Cl models.

TABLE I

THE MULLIKEN-CHARGE ANALYSIS OF FAXM$_3$
CONVENTIONAL MODELS

STRUCTURES	Bond	Population (e)	Length (Å)
FAPbI$_3$	H$_2$-I$_2$	-0.03	2.90293
	H$_3$-I$_2$	-0.03	2.90294
	H$_4$-I$_2$	-0.12	2.82312
	H$_5$-I$_2$	-0.12	2.82313
FAPbBr$_3$	H$_2$-Br$_2$	-0.07	2.56729
	H$_3$-Br$_2$	-0.07	2.56729
	H$_4$-Br$_2$	-0.15	2.65160
	H$_5$-Br$_2$	-0.15	2.65159
	Br$_1$-Pb$_1$	-5.05	2.96425
FAPbCl$_3$	H$_2$-Cl$_2$	0.04	2.40074
	H$_3$-Cl$_2$	0.04	2.40074
	H$_4$-Cl$_2$	0.03	2.48088
	H$_5$-Cl$_2$	0.03	2.48088
	Cl$_1$-Pb$_1$	0.20	2.97605
	Cl$_3$-Pb$_1$	0.10	2.81745
	Cl$_2$-Pb$_1$	0.07	2.93028
FASnI$_3$	H$_2$-I$_2$	-0.05	2.79995
	H$_3$-I$_2$	-0.05	2.79961
	H$_4$-I$_2$	-0.14	2.78355
	H$_5$-I$_2$	-0.14	2.78315
FASnBr$_3$	H$_2$-Br$_2$	-0.09	2.52194
	H$_3$-Br$_2$	-0.09	2.52152
	H$_4$-Br$_2$	-0.19	2.57252
	H$_5$-Br$_2$	-0.19	2.57297
	Br$_1$-Sn$_1$	-1.20	2.89173
	Br$_2$-Sn$_1$	-2.13	2.98997
FASnCl$_3$	H$_2$-Cl$_2$	0.04	2.36003
	H$_3$-Cl$_2$	0.04	2.36034
	H$_4$-Cl$_2$	0.03	2.40618
	H$_5$-Cl$_2$	0.03	2.40628
	Cl$_2$-Sn$_1$	0.15	2.87758
	Cl$_1$-Sn$_1$	0.24	2.66347
	Cl$_3$- Sn$_1$	0.27	2.94575

Later, we launch the elastic constant (EC) calculations in order to check the mechanical stability for the optimized structures. In table. II demonstrate that the obtained EC results for all the lead and tin-based models, and these values are prominent to find the mechanical stability behavior of the structure. In order to get a stable structure, all the six orthorhombic (pseudo-cubic) models need to obey the following stability condition. [24]

$$C_{11} > 0, C_{11}C_{22} > C_{12}{}^2,$$
$$C_{44} > 0, \ C_{55} > 0, C_{66} > 0,$$
$$C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}{}^2 - C_{22}C_{13}{}^2 - C_{33}C_{12}{}^2 > 0. \tag{1}$$

The obtained EC results of all the six FA-based models confirm that the structure is mechanically stable. From table. II, we can recognize that the C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13}, and C_{23} values are varied based on the halide and the X site substitution. It might be relevent to the bonding between different halogen positions, especially their bond population and bond length values.

TABLE II

CALCULATED ELASTIC CONSTANT VALUES OF SIX DIFFERENT FA BASED PEROVSKITES

	c$_{11}$	c$_{22}$	c$_{33}$	c$_{44}$	c$_{55}$	c$_{66}$	c$_{12}$	c$_{13}$	c$_{23}$	ref
FAPbI$_3$	40.6	48.2	32.4	0.9	1.4	1.7	8.4	10.4	7.0	this work
FAPbI$_3$	30.1	31.0	29.8	2.0	5.3	2.6	2.9	7.2	4.2	[15]
FAPbI$_3$	20.5			4.8			12.3			[12]
FAPbBr$_3$	47.4	54.2	40.5	0.8	1.5	3.0	9.7	11.2	6.7	this work
FAPbBr$_3$	37.9	45.2	34.5	3.3	5.3	1.8	7.2	9.9	5.6	[15]
FAPbCl$_3$	54.1	61.8	44.1	1.2	1.8	1.5	11.3	13.9	8.7	this work
FASnI$_3$	26.1	48.7	40.4	4.3	1.6	5.7	9.3	6.8	5.4	this work
FASnI$_3$	29.9	25.2	26.0	2.3	4.9	2.4	6.8	8.2	3.2	[15]
FASnBr$_3$	47.3	52.9	42.6	0.7	1.7	2.3	9.2	12.6	6.8	this work
FASnBr$_3$	35.3	25.6	32.1	3.2	5.6	1.2	5.7	10.8	3.7	[15]
FASnCl$_3$	18.5	52.2	23.9	1.1	1.9	1.8	10.9	13.3	7.2	this work

We observed that C_{66} value is relatively more significant than C_{44} and C_{55}, which indicates that there is a stronger coupling between the direction a and b than a and c or b and c. The obtained results may be varied from the Pb and Sn or different halide (I, Br, and Cl) substitution in FA perovskite structure. Our calculated EC values are slightly larger than the data calculated by L. Geo *et al.* [15]. They investigated the elastic moduli behavior for FA cation based perovskites, and their findings explain that Br-based perovskites have durable anisotropic nature than I-based perovskites. Also, they demonstrate that replacing Br instead of I either with Pb or Sn perovskite models, which significantly reduces the bulk modulus, shear modulus, and Young's modulus values. Besides, J. F. Wang *et al.* demonstrate that the primary interaction occurred between the organic FA cation and inorganic framework (Pb or Sn and I, Br, and Cl) is through the ionic bonding between NH$_2$ and I ions, which might decide the stability. [12] Therefore, based on the chosen element and substitution site, determine the structural and mechanical behavior. Further depth investigation is needed to understand both the stability mechanism and the structural behavior for organic-inorganic perovskites absorber layer.

IV. CONCLUSIONS

In summary, the structural and mechanical stability behavior was systematically analyzed for all the organic FA cation based,

six different configurations inside the inorganic cage (Pb or Sn with I, Br, and Cl). Our results demonstrate that the lattice parameter values decreasing for Br and Cl based models compared to I-based perovskite models. The MC analysis exhibits that the halogen to FA cation bonding influence the EC results, especially H_4 and H_5 to X_2 (where I_2, Br_2, and Cl_2). Meanwhile, we did not observe any bond population between the Pb or Sn to the I halogen in $FAPbI_3$ and $FASnI_3$ models. Our obtained EC result shows that all six conventional pseudo-cubic models are mechanically stable. Our findings might be helping to understand the FA cation based perovskite absorber layer structural and stability behavior.

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