Isosymmetric compression of cubic halide perovskites ABX_3 ($A = K, Rb, Cs$; $B = Ge, Sn, Pb$ and $X = Cl, Br, I$)-influence of cation–anion exchange: a first principle study

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Abstract

Halide perovskites are potential candidates for their use in solar cells. In this study, an investigation of the structural, mechanical and electro-optical properties of ABX_3 ($A = K, Rb, Cs$; $B = Ge, Sn, Pb$ and $X = Cl, Br, I$), under isosymmetric compression, is presented. All the calculations are performed with generalized gradient approximation schemes. We have examined the effect of cation and anion substitution on their overall properties.

Keywords Halide perovskites · DFT calculations · Isosymmetric compression · Structural-mechanical properties · Electro-optical properties

1 Introduction

Halide perovskites, ABX_3 (A is a monovalent cation, B is a bivalent cation and X is a halogen) are found to be important ternary materials for potential use in optoelectronic and photovoltaic applications due to their efficient light-harvesting capabilities [1–4]. Their inherent direct band gap, which resemble the solar spectrum qualify them as excellent solar cell materials [5, 6]. Recent studies of halide perovskites have reported the power conversion efficiency above 25% for perovskite-based solar cells [7].

Despite the tunable band gap, large absorption coefficient in the visible spectrum with long charge carrier diffusion length, small exciton binding energy, defect resistance enabling non-radiative recombination and low-cost fabrication process for perovskite solar cells than conventional cells, they show instability with even minor external conditions and thereby degrade swiftly, decreasing the power conversion efficiency [8–16]. A number of measures have been taken by various researchers not only to

make them stable but also tune the band gap at the same time [17–19]. Among several measures, the application of pressure is considered to be one of the clean and green ways to nullify such problems. Furthermore, the investigation of the influence of the reorganization on the lattice structure and its implications on the electronic structure of perovskites can be understood by applying pressure at different scales.

The application of pressure on perovskites can cause several effects, such as dilation of the lattice [20], displacement of cation and anion [21, 22], rotation of octahedral cages [23], phase transitions [24, 25], etc. Generally, more than one effect can occur in perovskites at a time, leading to the dependence of the electronic structure calculations on a number of factors. It is, therefore, critical to study the effect of each factor individually by isolating other effects. Such a study will be beneficial in identifying one-to-one understanding of the dynamics of electronic structure configuration and the properties that are associated with it.

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A number of papers on perovskites in the literature discuss about the effects of lattice dilation and octahedral rotations [26–28]. The significance of the present study is that it focuses only on the lattice dilation, keeping octahedral rotations unchanged, in the aftermath of the hydrostatic pressure. For this purpose, we have chosen to study the influence of hydrostatic pressure on halide perovskites to investigate how the lattice dilation would affect the electronic structure and the associated properties without any rotation of the polyhedra or phase transitions. Such an application of pressure here on is called isosymmetric compression and the choice of materials that are used to study the isosymmetric lattice contraction are cubic (space group Pm3m) ABX_3 where $A = K, Rb, Cs$; $B = Ge, Sn, Pb$ and $X = Cl, Br, I$. The chosen halide perovskites are taken in such a way that their respective cation and anion belong to the same group (A =alkali metal, B =crystallogen and C =halogen). This way of selecting the perovskites is advantageous as it not only facilitates the study of size effect but also hinders the charge effect as one moves down the periodic table.

The stability and degree of distortion in perovskites are usually quantified by the Goldschmidt tolerance factor (t) [29],

$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)} \quad (1)$$

where, R_A , R_B and R_X are the radii of A , B and X , respectively, and the measured octahedral tilt angle. In the case of isosymmetric compression, it is easy to note that the tolerance factor for all cubic distorted structure, under compression, should be constant close to unity and exhibits no octahedral tilt or $a^0a^0a^0$ in terms of Glazer notation [30].

In this paper, the various aspects of isosymmetric effects have been discussed. We have investigated the structural, mechanical and electro-optical properties of halide perovskites under isosymmetric lattice contraction. Further, the size effects due to cation and anion substitution have been explored in detail. It is anticipated that the results of this type of study will be beneficial to design future materials.

2 Computational methods

The first principles calculations based on Density Functional Theory (DFT) have been implemented using the Vienna Ab initio Simulation Package (VASP) [31–33]. The calculations were performed within the Generalized Gradient Approximation (GGA) using Perdew, Burke and Ernzerhof (PBE) [34, 35] as exchange-correlation functional. This approach considers the valence

states $3s^23p^64s^1$ for K , $4s^24p^65s^1$ for Rb , $5s^25p^66s^1$ for Cs , $3d^{10}4s^14p^2$ for Ge , $5s^25p^2$ for Sn , $5d^{10}6s^26p^2$ for Pb , $3s^23p^5$ for Cl , $4s^24p^5$ for Br and $5s^25p^5$ for I . All the lattice optimization for cubic structures were performed with a convergence criterion that the final force acting on each atom should not exceed $0.015 \text{ eV}/\text{\AA}$. A large Monkhorst K-mesh with spacing of $0.06 \text{ \AA}^{-1}$ and the plane-wave basis functions with cut off energy of 410 eV were considered. The Gaussian smearing of width 0.05 eV was carried out for Brillouin zone integration except for density of states calculations where tetrahedron method with Blöchl corrections was used. The electronic band structures were calculated by considering both spin-orbit coupling (SOC) and without spin-orbit coupling (WSOC). The hydrostatic pressure was applied from 1 GPa – 10 GPa and optimization of the pressure induced structures were implemented with total energy convergence tolerance of $1.5 \times 10^{-9} \text{ eV}$ and force convergence tolerance of $0.0154 \text{ eV}/\text{\AA}$. All the simulations were performed by imposing the symmetry preserved constraint, as this study is focused on isosymmetric lattice contraction. For the simulations of the mechanical properties, the elastic stiffness constants, matrices $[C_{ij}]$, were computed using the stress-strain relationships for all the pressure induced optimized structures [36]. The bulk modulus B and the shear modulus G were calculated from the matrix $[C_{ij}]$ using the Voigt-Reuss-Hill (VRH) averaging scheme [37, 38],

$$B_v = B_R = \frac{C_{11} + 2C_{12}}{3} \quad (2)$$

$$B = \frac{1}{2}(B_v + B_R)$$

$$G_v = \frac{C_{11} - C_{12} + 3C_{44}}{5}$$

$$G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})} \quad (3)$$

$$G = \frac{1}{2}(G_v + G_R)$$

The bulk modulus was also calculated by fitting the pressure-volume (P - V) data points using the Birch–Murnaghan 3rd order equation of state [39],

$$P(V) = \frac{3B}{2} \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] \times \left[1 + \frac{3}{4}(B' - 4) \left(\left(\frac{V_0}{V} \right)^{2/3} - 1 \right) \right] \quad (4)$$

where V_0 is the equilibrium volume and $B' = \frac{dB}{dP}$. The mechanical nature of all these structures were quantified by measuring Pugh ratio (B/G) and normalized Cauchy

pressure ($\frac{C_{12} - C_{44}}{E}$), where E is the Young's modulus calculated as in [40],

$$E = \frac{9BG}{3B + G} \quad (5)$$

The optical properties were analyzed for all the pressure induced structures by calculating the frequency (ω) dependent dielectric functions, $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, where imaginary part is calculated as,

$$\epsilon_2(\omega) = \frac{e^2 \hbar}{\pi m^2 \omega^2} \sum_{v,c} \int_{\text{BZ}} |M_{cv}(k)|^2 \delta[\omega_{cv}(k) - \omega] d^3k \quad (6)$$

where M_{cv} is the momentum matrix for a vertical transition from a filled initial state to an empty final state. The corresponding real part is calculated from the imaginary part using Kramers–Kronig transformation. Likewise, the estimation of the optical parameters, such as the absorption coefficient (α), reflectivity (R) and refractive index (n) were done according to the relations [41–43],

$$\alpha(\omega) = \frac{2\omega}{c} \left[\frac{\{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)\}^{1/2} - \epsilon_1(\omega)}{2} \right]^{1/2} \quad (7)$$

$$n(\omega) = \left[\frac{\{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)\}^{1/2} + \epsilon_1(\omega)}{2} \right]^{1/2} \quad (8)$$

$$R(\omega) = \frac{(n-1)^2 + \left(\frac{\alpha c}{2\omega}\right)^2}{(n+1)^2 + \left(\frac{\alpha c}{2\omega}\right)^2} \quad (9)$$

where c is the speed of light.

3 Results and discussion

We have selected cubic halide perovskites ABX_3 ($A = K, Rb, Cs$; $B = Ge, Sn, Pb$ and $X = Cl, Br, I$) and studied how their structures and electro-optical properties vary due to the exchange of cation and anion in their respective group of the periodic table, under the influence of isosymmetric compression. The lattice parameter (a_0), band gap (E_g) and bulk modulus (B) of various optimized structures along with their corresponding available experimental and theoretical values are shown in Table 1. Our calculated lattice parameters overestimate experiment by 2%, as expected given that they were calculated using the PBE. Likewise, the band gap severely underestimates experiment under WSOC by 9–49% and the underestimation is even worse due to SOC. The reason for the closer proximity of WSOC may be due to a fortuitous error cancellation between the neglect of quasi-particle correction and spin–orbit coupling. However, since we are only interested in trends, this underestimation is not problematic.

Further, the bulk modulus values obtained by fitting the third-order Birch–Murnaghan Eq. 4 match well with those calculated from elastic tensor matrices. The bond length variations of $A-X$ and $B-X$ along with their compressibilities were calculated to quantify whether the simulations yield optimized isosymmetric structures for all cubic compressed structures. The variations in bond lengths with pressure are shown in Fig. 1, which satisfy the condition $\langle A-X \rangle = \sqrt{2} \langle B-X \rangle$. Similarly, from the compressibility point of view, it is hitherto understandable that the compressibility of polyhedron AX_{12} should match with the polyhedron BX_6 under isosymmetric compression. Their variations are also shown in Fig. 2, which implicitly yields the

Table 1 The calculated values of lattice parameters (a_0), energy gap (E_g) and bulk modulus (B). The experimental/theoretical values are given with the citation number in parentheses

Materials	a_0 (Å)		E_g (eV)			B (GPa)	
	This work	Literature	This work WSOC	This work SOC	Literature	This work	Literature
$CsPbCl_3$	5.714	5.605 ^a [44]	2.27	1.10	3.0 ^a [45]	23.690 ^c , 23.464 ^d	21.54 ^b , 22.59 ^b , 31 ^b , 25.8 ^b [46]
$CsPbBr_3$	5.989	5.87 ^a [44]	1.87	0.69	2.25 ^a –2.30 ^a [45, 47]	18.845 ^c , 18.956 ^d	18.45 ^b , 27 ^b , 23.5 ^b [46]
$CsPbI_3$	6.384	6.289 ^a [44]	1.59	0.35	1.73 ^a [48]	14.904 ^c , 14.998 ^d	14.38 ^b , 14.4 ^b , 19.8 ^b , 23 ^b [46]
$CsGeI_3$	5.991	5.98 ^a –6.05 ^a [3, 44]	0.83	0.4	1.63 ^a [49]	17.824 ^c , 18.265 ^d	18.89 ^b [46]
$CsSnI_3$	6.273	6.219 ^a [44]	0.68	0.08	1.31 ^a [50]	15.22 ^c , 15.754 ^d	15.10 ^b , 17.59 ^b , 6.30 ^b [51]
$KPbI_3$	6.337	6.352 ^b [52]	1.54	0.28	1.36 ^b [52]	15.261 ^c , 15.939 ^d	-
$RbPbI_3$	6.359	6.366 ^b [52]	1.57	0.31	1.37 ^b [52]	15.536 ^c , 15.284 ^d	-

^aExperimental value of room-temperature phase

^bTheoretical value of cubic phase; obtained using ^cThird-order Birch–Murnaghan EOS, ^dElastic tensor matrix

Fig. 1 The bond length variation under isosymmetric lattice contraction

Fig. 2 The variation of compressibility of the polyhedra due to isosymmetric compression

condition for isosymmetric cubic structure contraction as $V_{A-X} = 3.24 \times V_{B-X}$, where V_{A-X} and V_{B-X} are the volumes of polyhedra AX_{12} and BX_6 , respectively.

The structural variations of lattice parameters of these perovskites, under hydrostatic pressure, are highlighted in Fig. 3. The lattice parameter varies inversely with compression and it can be seen that a quadratic model of the form $a(P) = a_0 + c_1P + c_2P^2$ can be used to describe the variation, where a_0 is the equilibrium lattice parameter, c_1 and c_2 are negative and positive coefficients, respectively. One can further notice that the size of the atomic radius contributes significantly to the variation of the lattice parameters. For the size of atomic radius $K < Rb < Cs$, $Ge < Sn < Pb$ and

$Cl < Br < I$, the order of variations in lattice parameters are $KPbI_3 < RbPbI_3 < CsPbI_3$, $CsGeI_3 < CsSnI_3 < CsPbI_3$ and $CsPbCl_3 < CsPbBr_3 < CsPbI_3$, respectively. This is due to the fact that there is no contribution of bonding to lattice variation in those structures as these alkali metals, crystallogens and halogens have the same number of valence electrons down their respective groups of the periodic table. The size of cation and anion is also associated with the compressibility. The smaller the size, the smaller the bond lengths $\langle A-X \rangle$ and $\langle B-X \rangle$, which in turn results in smaller compressibility. The compressibility in perovskites is usually dominated by the bond length $\langle A-X \rangle$ due to the larger volume of the polyhedron $[A-X]_{12}$. However, for isosymmetric contraction,

Fig. 3 The lattice parameter variation as a function of the isosymmetric compression

both $\langle A-X \rangle$ and $\langle B-X \rangle$ play equal role as shown earlier in Fig. 2. Thus, it can be said that CsPbCl_3 shows more resistance to deformation than CsPbBr_3 and CsPbI_3 because of its smaller size anion and the order follows in accordance with the size of their respective anions ($\text{Cl} < \text{Br} < \text{I}$). Likewise, similar comparison can be drawn for the remaining perovskites based on the size of their respective cations. The effect of size can also be seen in the mechanical behavior of these materials. For instance, due to the higher compressibility, CsPbI_3 is softer and more ductile than CsPbBr_3 and CsPbCl_3 . In other words, CsPbI_3 can withstand fracture longer than CsPbBr_3 and CsPbCl_3 under compression. Their deformation behavior can also be quantified by measuring Pugh ratio and normalized Cauchy pressure [53]. The Pugh ratio criterion [54] suggests that the materials show ductile nature when B/G ratio is greater than 1.75; otherwise, they exhibit brittle nature. Likewise, the Pettifor criterion [55] suggests that the materials develop covalent character when the Cauchy pressure is negative and hence possess brittle nature and vice versa. The result is shown in Fig. 4. According to Pugh ratio and Cauchy

pressure criteria, except CsGeI_3 , all of them show ductile character and ductility increases under isosymmetric compression. Therefore, the transition of materials from brittle character to ductile character might be achieved by the application of compression. According to the Pettifor criterion, CsGeI_3 shows greater tendency for directional bonding and therefore makes this material brittle. Moreover, one can notice that the red line is the longest among other ductile materials indicating that the associated material can rupture quicker during compression and the presence of discontinuity in the lines can be interpreted as the change in the nature of the bonding.

It has been observed that the alteration of cation and anion size contributes significantly to the macroscopic elastic properties. The very next implication would be the change in the electro-optical behaviors resulting from this alteration. The electronic behavior can be studied by performing the band structure computations along the high symmetric path. As an example, due to the smaller size of the Cl atom, the lattice volume of CsPbCl_3 is the smallest among CsPbBr_3 and CsPbI_3 . As a result, the volume of reciprocal space or the Brillouin zone (BZ) follows the order

Fig. 4 The brittle/ductile nature interpreted in terms of Pugh ratio and normalized Cauchy pressure

$CsPbCl_3 > CsPbBr_3 > CsPbI_3$. This effect has been shown by the dashed lines in the plots of Fig. 5. The dashed lines indicate that the resulting position of high symmetric K-points of $CsPbI_3$ is mapped in the band structures of the remaining perovskites. Furthermore, due to compression, there is an increment of the Brillouin zone which can be seen from the position of dashed curves (in red and cyan color) in the band structures. One can notice that, all these perovskites are direct band gap materials with transition occurring at $R-R$ symmetric points. Under isosymmetric compression of these structures, the band gap remains direct but reduces, thereby altering the semiconductor behavior towards metallic nature. It should be noted that the computed band structures in Fig. 5, do not consider SOC. This is because the simulated band gap is worsened more by considering SOC than WSOC and, under isosymmetric compression, there is a probability of reducing the band gap to negative values. The density of states (DOS) and the individual contribution of each element or partial density of states (PDOS), in Fig. 6, shows clearly that the hybridization of s orbital of B and p orbitals of X contribute to the valence band maxima (VBM), whereas the conduction band minima (CBM) is dominated by p orbitals of B . Further, the antibonding of $B-s$ and $X-p$ at VBM is significant resulting in covalent nature of the overlap. Unlike in VBM, the overlap in CBM has ionic nature as the band is singly dominated by p orbitals of B . Therefore, based on the analysis of DOS, the size of anion can influence the tuning of band gap in these halide perovskites in a definite order. For instance, the band gap varies in the order of $CsPbCl_3 > CsPbBr_3 > CsPbI_3$ indicating that the larger size of anion results in redshift of the band gap. However, the effect of cation size of alkali elements in the PbI framework

shows increase in the band gap ($KPbI_3 < RbPbI_3 < CsPbI_3$) with respect to size. Similarly, it is interesting to note that there is no definite size effect due to crystallogenic cations in the band gap- as the band gap varies in the order of $CsSnI_3 < CsGeI_3 < CsPbI_3$, whereas size varies in the order of $Ge < Sn < Pb$. These trends of band gap variation, with respect to the order of the size of A cation and X anion, are the same with or without SOC. However, they are different for B cation. The variation of band gap under SOC follows the order $CsSnI_3 < CsPbI_3 < CsGeI_3$. This may be due to higher SOC corrections ($\Delta E_g^{SOC} = E_g^{SOC} - E_g^{WSOC}$) in $CsPbI_3$, which is 81% greater than $CsGeI_3$, as shown in Fig. 7. The other possibility can be the choice of exchange-correlation functional or method implemented, which results in different magnitudes of quasi-particle corrections in these systems. In the work of Huang and Lambrecht [44], they have shown that the band gap follows the order $CsSnI_3 < CsGeI_3 < CsPbI_3$, under both SOC and WSOC, using quasi-particle self-consistent GW method. However, these conformities are violated, when anion I is replaced by anion Cl ; plus all their results (trends of variation) agree with our under WSOC formalism. As the cubic phases of these perovskites are unstable at the room temperature, it is very difficult to reckon the correct trend experimentally. Nevertheless, we have compared with their room-temperature phases and found that the trends in all the cation and anion variations do satisfy with the trends calculated under WSOC.

All these variations can be explained based on the degree of overlap between $B-s$ and $X-p$ orbitals. For instance, one can notice from Fig. 6 that the overlap in Sn-perovskite is more than that of Ge-perovskite and Pb-perovskite, suggesting that the band gap follows the order

Fig. 5 Electronic band structure of cubic halide perovskites in the high symmetric path under different pressure. The vertical dashed lines, except CsPbI_3 , are used to denote high symmetric K-points of CsPbI_3 mapped into BZ of other perovskites

of $\text{CsSnI}_3 < \text{CsGeI}_3 < \text{CsPbI}_3$. Based on this observation, it can be said that the greater ionic nature of hybridization between B -s and X -p orbitals results in blueshift of the band gap in halide perovskites. Further, the influence of compression on the lattice has been observed by the redshift of DOS with increasing pressure.

For the optical properties, we have chosen independent particle approximation (IPA) to study optical parameters, such as absorption coefficient (α), reflectivity (R)

and refractive index (n), under isosymmetric compression. One can notice from Fig. 8 that all these materials show good absorption in the visible spectrum. The application of pressure increases the absorption coefficient towards low band gap. In contrast, reflectivity and refractive index are high at the beginning indicating opacity for time-independent field. Likewise, the variation of refractive index can be interpreted based on the band gap. The computed static refractive index implies qualitatively that it varies

Fig. 6 The density of states showing TDOS and PDOS of X and B with their orbitals contributions

inversely with the band gap and the order of refractive index $ABl_3 > ABBr_3 > ABCl_3$ can be explained as the larger size of anion I has comparatively more loose electrons

resulting in higher degree of polarizability. As the accuracy of DFT calculations rely on the choice of exchange-correlation potential, the underestimation of band gap can also

Fig. 7 Doubly degenerate conduction bands due to SOC. The magnitudes of spin–orbit splitting increases from Ge to Pb

be thought as the overestimation of refractive index. For instance, our computed static refractive index for CsPbBr_3 and CsPbI_3 overestimate their experimental counterparts roughly by 8 and 14%, respectively [56, 57]. Similarly, the effect of compression on these optical parameters can also be explained based on the shrinkage of the band gap. It can be seen that, under isosymmetric compression, materials with less band gap have higher optical parameters

till the visible region and the pattern becomes opposite towards the ultra-violet region. On the other hand, one can qualitatively imply that the larger band gap materials show less optical response, even during compression.

4 Conclusions

To the best of our knowledge, this study has explored the idea of isosymmetric lattice compression for the first time in perovskites. We have studied the aftermath of the isosymmetric lattice compression in seven halide perovskites and some of the key findings are as follows: (a) the Goldschmidt tolerance factor remains unchanged, (b) the degree of compressibility of polyhedra AX_{12} matches well with their corresponding polyhedra BX_6 , (c) the volume of these polyhedra satisfies the relation, $V_{\text{A-X}} = 3.24 \times V_{\text{B-X}}$, and (d) band gap decreases but the compression preserves the band gap nature. Since the changes in properties of perovskites emerge from the competition between octahedral tilt and lattice contraction, the study of isosymmetric lattice compression is significant as it isolates octahedral tilt. Further, the size reduction due to A cation and X anion is accompanied by the widening of band gap, and there is no definite pattern in the band gap variation due to B cation. It is observed that band gap widening is caused by a decrease in overlap between B-s and X-p and vice versa. From this study, one can remark that the overlap between B-s and X-p increases with isosymmetric lattice contraction, implying that such changes may have been anomalous if the octahedral tilting is taken into account. Moreover, the study has qualitatively shown the inverse relation between band gap and refractive index with the larger band gap materials showing less optical response. All the studied materials have intrinsic direct band gap matching the solar spectrum and show good absorption for the visible spectrum. These photonic qualities can be further enhanced with isosymmetric strains. The application of isosymmetric stress resists the external conditions and therefore allows these potent solar materials to behave predictably. Such information may be useful to design optoelectronic devices, such as LEDs, solar cells, etc.

Fig. 8 Optical spectra—absorption coefficient (α), reflectivity (R) and refractive index (n) as a function of pressure. Solid line represents normal conditions

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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