The Effect of Structural Phase Transitions on Electronic and Optical Properties of CsPbI$_3$ Pure Inorganic Perovskites

Rahmad Syah $^{1, *}$, Afshin Davarpanah $^{2, *}$, Mahyuddin K. M. Nasution $^{3, *}$, Qamar Wali $^{4, *}$, Dadan Ramdan $^{1}$, Munirah D. Albaqami $^{5}$, Mohamed Ouladsmane $^{5, *}$ and Saja Mohammed Noori $^{6}$

Abstract: Hybrid inorganic perovskites (HIPs) have been developed in recent years as new high-efficiency semiconductors with a wide range of uses in various optoelectronic applications such as solar cells and light-emitting diodes (LEDs). In this work, we used a first-principles theoretical study to investigate the effects of phase transition on the electronic and optical properties of CsPbI$_3$ pure inorganic perovskites. The results showed that at temperatures over 300 °C, the structure of CsPbI$_3$ exhibits a cube phase (pm3m) with no tilt of PbI$_6$ octahedra (distortion index = 0 and bond angle variance = 0). As the temperature decreases (approximately to room temperature), the PbI$_6$ octahedra is tilted, and the distortion index and bond angle variance increase. Around room temperature, the CsPbI$_3$ structure enters an orthorhombic phase with two tilts PbI$_6$ octahedra. It was found that changing the halogens in all structures reduces the volume of PbI$_6$ octahedra. The tilted PbI$_6$ octahedra causes the distribution of interactions to vary drastically, which leads to a change in band gap energy. This is the main reason for the red and blue shifts in the absorption spectrum of CsPbI$_3$. In general, it can be said that the origin of all changes in the structural, electronic, and optical properties of HIPs is the changes in the volume, orientation, and distortion index of PbI$_6$ octahedra.

Keywords: hybrid inorganic perovskites; distortion index; octahedral volume; distribution of interaction; bond angle variance; solar cells

1. Introduction

Lead halide-based perovskites have been widely studied as absorbing materials for thin film solar cells with a power conversion efficiency of about 20%, [1–14]. These compounds can also be used as a promising emitter in light-emitting diodes (LEDs) [15–28]. The general chemical formula for HIPs is ABX$_3$, where A is a monovalent inorganic cation, similar to Cs$^+$: cesium; X is a halogen anion including F$^-$, I$^-$, Br$^-$, and Cl$^-$, and B is a divalent metallic cation such as Pb$^{2+}$, Sn$^{2+}$, Cu$^{2+}$, etc. [29–42]. Inorganic hybrid perovskites have a semiconducting nature. In all types of hybrid perovskites, divalent metallic cations form a BX$_6$ octahedral with halogen anions [43–56]. Most of the electronic and optical properties of hybrid perovskites depend on the BX$_6$ framework [57–70]. These materials are found in an orthorhombic phase at low temperatures (space group: Pnma) [71–84]. As the temperature increases to about 50 °C, the structure of HIPs takes a tetragonal phase with the space group P4/mmb, and at temperatures above 300 °C, they are in the original
cubic phase with the space group Pm3m. In hybrid perovskite structures, by changing the halogens from iodine to bromine and then chlorine, the BX$_6$ octahedral volume decreases, resulting in a reduction in total volume of the structures [85–90]. To acquire a comprehensive knowledge of the electrical and optical properties of semiconductor compounds, the band structure, electron density, charge carrier mobility, density of states, and dielectric function must be investigated [91–95].

The study of the characteristics of organic/inorganic hybrid perovskites suggests that these materials might be a viable alternative to semiconductor materials such as silicon, as well as semiconductor compounds such as Cu-InGeS (CIGS) and CuZnSnS (CZTS), which are extensively used in various optoelectronic devices [96–100]. Recent advances in the synthesis of inorganic hybrid perovskite nanostructures have increased the importance of HOIPs [101–108].

Due to their special properties such as broadband infrared absorption, narrow PL emission bandwidth, high photoluminescence (PL), quantum yield (QY) Φ$_{PL}$, adjustable emission across the visible range, and desirable optical gain combined with low-threshold spontaneous emission, inorganic cesium lead halide perovskite colloidal quantum dots (CsPbX$_3$ QDs, X = Cl, Br, I) have attracted considerable attention in many applications of solar cells, LEDs, lasers, and photodetectors [109–111]. However, the chemical stability of CsPbX$_3$ QDs remains a serious issue, particularly for infrared applications. Indeed, the low chemical stability of APbX$_3$ (where A = (CH$_3$NH)$_3^+$, or HC(NH$_2$)$_2^+$; X = Br$^-$, I$^-$, and/or Cl$^-$) is the major impediment to the industrialization of corresponding devices as well as fundamental research into these compounds [112,113]. Obviously, more research into the structural and electrical properties, phase, and single crystals of these appealing semiconductor compounds can lead to the best use of their benefits in diverse applications while also improving their disadvantages [114,115].

In this work, we investigated the behavior of PbI$_6$ inorganic octahedral upon changing the structural phases of CsPbI$_3$ and assessed the contribution of the pb-I framework to the electronic and optical properties of CsPbI$_3$.

2. Computational Details

The PWSCF code, as implemented in the Quantum-Espresso package, was used for all computations [58]. Within a generalized gradient approximation, the Perdew–Burke–Ernzerhof exchange-correlation functional [59] was employed (GGA). The cubic and orthorhombic phases of pure inorganic perovskite materials with the chemical structure CsPbI$_3$ were the focus of our research. The density of valence electrons and wave functions were represented using scalar relativistic ultra-soft and plane-wave basis set pseudo-potentials. Wave functions and electron density were also represented using energy cutoffs of 35 and 330 Rydberg, respectively. A 12 $\times$ 12 $\times$ 12 Monkhorst–Pack grid [115–119] was selected for sampling the Brillouin zone (BZ) of the cubic systems. The structure was totally relaxed until each atom’s force was less than 0.0025 eV·Å$^{-1}$. We initially computed the frequency-dependent complex dielectric function to assess the optical properties [116].

$$\varepsilon(\omega) = 1 + \frac{8\pi}{\Omega N_k} \sum_{\kappa, \nu, c} \frac{|\langle \phi_{\kappa\nu} | \hat{v} | \phi_{\kappa c} \rangle|^2}{(E_{\kappa c} - E_{\kappa\nu})^2 (E_{\kappa c} - E_{\kappa\nu} - \omega - i\eta)}$$

(1)

where $\Omega$ is the cell volume, $N_k$ is the total number of k-points in the BZ, $\hat{v}$ is the operator of velocity, and $\eta$ is an opportune broadening factor. The indices $v$ and $c$ represent the occupied and unoccupied states, respectively.

It is feasible to acquire the whole dielectric tensor calculated on the imaginary frequency axe $\varepsilon(i\omega)$ by applying a London transformation on $\varepsilon(i\omega)$ [58].

$$\varepsilon(i\omega) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{\omega' \varepsilon(\omega')}{\omega'^2 + \omega^2} d\omega$$

(2)
The LOSS spectrum is proportional to the imaginary part of the inverse dielectric tensor [58]:

\[
\text{Imm}\left\{ \frac{1}{\varepsilon(\omega)} \right\} = \frac{\varepsilon_i(\omega)}{\varepsilon_r^2(\omega) + \varepsilon_i^2(\omega)}
\]

(3)

The refractive index, \(n(\omega)\) was calculated using the following formula:

\[
n(\omega) = \omega \sqrt{\frac{\varepsilon_r(\omega) + \varepsilon_r^2(\omega) + \varepsilon_i^2(\omega)}{2}}
\]

(4)

The frequency dependent absorption coefficient, \(\alpha(\omega)\), was also computed using the following relationship:

\[
\alpha(\omega) = \omega \sqrt{-\varepsilon_r(\omega) + \varepsilon_r^2(\omega) + \varepsilon_i^2(\omega)}
\]

(5)

3. Results

Figure 1 schematically illustrates the three-dimensional structure of the CsPbI\(_3\) inorganic perovskite in the cubic and orthorhombic phases. At temperatures above 300 °C, the CsPbI\(_3\) structure is in the cubic phase (Figure 1a). However, as the temperature decreases to around room temperature, the structure of the inorganic perovskite undergoes a phase transition and finds an orthorhombic phase at 25 °C (Figure 1b). The lattice parameters, band gaps, total structure volumes, and optimization energies are provided for both cubic and orthorhombic phases in Table 1. As can be seen, the volume of the CsPbI\(_3\) structure increases several times when the structural phase is transformed from cubic into orthorhombic. According to Table 1, the semiconductor nature of the pure inorganic perovskite is preserved during the structural phase transition caused by the temperature change. This can be attributed to the appropriate ratio of the lead atoms to the cesium and iodine atoms in each structural phase.

Figure 1. Schematic structure of CsPbI\(_3\) for: (a) Cubic phase and (b) Orthorhombic phase.
Table 1. Lattice parameters, structure volumes, band gap values, and optimization energies of CsPbI\textsubscript{3} for both cubic and orthorhombic phases.

| Component               | Lattice Parameter (Å) | Band Gap (eV) | Volume (Å\textsuperscript{3}) | Optimization Energy (eV) |
|-------------------------|-----------------------|---------------|-------------------------------|--------------------------|
| CsPbI\textsubscript{3} – Cubic | a = b = c = 6.40       | 1.62          | 262.97                        | −5265.40                  |
| CsPbI\textsubscript{3} – Orthorhombic | a = 10.53, b = 4.87, c = 18.07 | 2.45          | 927.092                       | −4223.486                 |

The band structure was calculated for both structural phases and is shown in Figure 2. When the CsPbI\textsubscript{3} structure is in the original cubic phase, we have a direct band gap at transition points R and M of the Brillouin zone (Figure 2a). Unlike conventional semiconductors such as GaAs, which have a dual degeneracy in the valence band maximum (VBM) range, in pure inorganic perovskite semiconductors, band degeneracy occurs in the conduction band minimum (CBM) range. This is a unique feature for these materials, which can be very useful in optoelectronic applications. Most electron transitions in the cubic phase are from the direct transition point R. When the structural phase changes to the orthorhombic, the band gap increases to about 2.50 eV. This is due to the increased interactions of cesium atoms with PbI\textsubscript{6} octahedra within the structure. Due to the change of the band structure pathway, the electron transitions in the orthorhombic phase occur at points X, B, and G. There is dual degeneracy at the G transition point, but at the B and X points, there is a small band splitting in the CBM range.

![Figure 2](image-url)  
**Figure 2.** Calculated band structure of the pure inorganic perovskite, (a) CsPbI\textsubscript{3} – cubic, (b) CsPbI\textsubscript{3} – Orthorhombic.

To determine the contribution of each atomic orbital to the interactions, the partial density of states (PDOS) was calculated for both cubic and orthorhombic phases and shown in Figure 3. From Figure 3a, it is clear that for the cubic phase, the 5p orbital of iodine atoms has the largest contribution to the DOS in the VBM range, and the 6p orbital of lead atoms has the most contribution in the CBM range. The cesium atom also plays a major role in the middle of the conduction band. The PDOS diagram shows that by changing the structural phase from the cubic to orthorhombic, the p orbital of iodine in VBM and the p orbital of the lead atom in CBM have still the most contribution to the DOS (Figure 3b). However, due to the increased interactions between the Cs atom and the PbI\textsubscript{6} inorganic octahedra, the band gap value increases (see Table 1).
Figure 3. Calculated DOS of the pure inorganic perovskite in VBM and CBM: (a) CsPbI$_3$ – Cubic, (b) CsPbI$_3$ – Orthorhombic.

To further investigate the structural phase transition of CsPbI$_3$ as well as the interactions between the inorganic Cs cation and the PbI$_6$ framework, the electron density was calculated in two and three dimensions, as shown in Figure 4. The ionic radii, atomic radii, Van Der Waals radii, and atomic masses of the atoms Cs, Pb, and I are listed in Table 2.

![Figure 4](image)

Figure 4. Two-dimensional (2D) and 3D depiction of electron density of the pure inorganic perovskite: (a) CsPbI$_3$ – Cubic, (b) CsPbI$_3$ – Orthorhombic.

Table 2. Ionic radii, atomic radii, Van Der Waals radii, and atomic masses of I, Pb, and Cs.

| Atom Name | Ionic Radius (Å) | Atomic Radius (Å) | Van der Waals Radius (Å) | Atomic Mass  |
|-----------|------------------|-------------------|--------------------------|-------------|
| I         | 2.2              | 1.33              | 1.98                     | 126.90      |
| Pb        | 1.19             | 1.75              | 2.16                     | 207.20      |
| Cs        | 1.74             | 2.72              | 3.31                     | 132.90      |
According to Figure 4a, in the cubic structural phase, the lead atom is located in the center of the PbI$_6$ framework and interacts with the cesium cation. From Table 3, it is expected that the cesium atom interacts more with the PbI$_6$ framework due to its larger interaction radius than the other atoms. However, from Figure 4, it can be seen that the cation Cs has little interaction with the inorganic octahedra. This is because of the type of interactions between the cation Cs and PbI$_6$, which is of the Van der Waals type. Therefore, Cs interactions do not have a large contribution to the DOS in VBM and CBM ranges, but they play the largest role in the high energy levels of the conduction band. Figure 4a shows that most of the interactions here occur between the lead and iodine atoms.

Table 3. Distance between the atoms inside the CsPbI$_3$ pure inorganic perovskite.

| Component   | Cubic Phase | Orthorhomic Phase |
|-------------|-------------|-------------------|
| Atom Name   | I (Å)       | Pb (Å)            | Cs (Å) | Atom Name   | I (Å)       | Pb (Å)            | Cs (Å) |
| I           | 4.53        | 3.20              | 4.53   | I           | 4.87        | 3.10              | 3.52   |
| Pb          | 3.20        | 0                 | 5.60   | Pb          | 3.10        | 7.84              | 5.44   |
| Cs          | 4.53        | 5.60              | 6.40   | Cs          | 3.93        | 5.44              | 5.97   |

The distortion index, bond angle variance, and PbI$_6$ octahedral volume are represented in Table 3 for the two structural phases of CsPbI$_3$. According to Table 3 and Figure 5, the distortion index and bond angle variance of the structure are zero in the cubic structural phase at high temperatures. This is due to the symmetry of the structure. As shown in Figure 5, as the temperature decreases, octahedra PbI$_6$ is tilted, and a bond angle variance of 19.0306$^\circ$ and a distortion index of 0.01817 Å are created. In fact, the main reasons for the structural phase transition caused by temperature changes are two important factors: the distortion index and bond angle variance, which affect the PbI$_6$ inorganic octahedra. From Figure 4b, it can be seen that the PbI$_6$ octahedra is tilted, which causes some disorders in the distribution of interactions between the Cs cation and the PbI$_6$ framework. According to the two-dimensional electron density (001), it is observed that similar to the cubic phase, the lead cation and iodine anion have the most contribution in the interactions. According to Figure 5 and Table 3, it is found that with changing the structural phase of CsPbI$_3$ from cubic to orthorhombic, the PbI$_6$ volume increases. The distance between the atoms comprising the structure is given in Table 4 for both phases. However, this structural phase transition has increased the interaction of CS cation with PbI$_6$ octahedra. This can be related to the increased volume and consequently the increased interaction radius of the Pb-I framework. From Table 4, it is evident that increasing the interaction radius of the Pb-I octahedra leads to a decrease in the distance between the cesium cation and the Pb-I framework. Therefore, the Van der Waals-type interactions between the cation Cs and the PbI$_6$ and consequently the band gap of the CsPbI$_3$ inorganic perovskite increase.

Table 4. Volume, distortion index, and bond angle variance of PbI$_6$ – Octahedral within the CsPbI$_3$ structure.

| Component            | Distortion Index (Å) | Bond Angle Variance (deg$^2$) | Volume (Å$^3$) |
|----------------------|----------------------|-------------------------------|---------------|
| CsPbI$_3$ – Cubic    | 0                    | 0                             | 43.82         |
| CsPbI$_3$ – Orthorhombic | 0.01817             | 19.306                        | 46.25         |
To investigate the optical properties of the CsPbI$_3$ structure, the real and imaginary parts of the dielectric function were calculated for both structural phases and shown in Figure 6. The computed static dielectric constant is reported in Table 5. As mentioned in the previous section, the band gap of the CsPbI$_3$ structure increases following the structural phase transition caused by a temperature change. In turn, this increase in the band gap value reduces the static dielectric constant value and also causes a blue shift in the first peak of the imaginary part of the dielectric function, which is also the location of the first electron transition. Indeed, this is due to the increased interactions between the cesium cation and inorganic PbI$_6$ octahedra. To confirm the accuracy of the static dielectric constant calculations, the $\varepsilon(\omega)$ spectrum was evaluated for both structural phases and shown in Figure 6b. It is clear that the starting point of this spectrum actually corresponds to the static dielectric constant. By changing the structural phase from cube to orthorhombic, this point drops to 3.42. According to the spectrum of electron energy loss, it is observed that at the location of the first peak, there is the least amount of electron energy loss, which is strong confirmation for the results obtained for the dielectric function.

**Figure 5.** Calculated average PbI$_6$ octahedral volume, average distortion index (bond length), and bond angle variance of CsPbI$_3$ for the cubic and orthorhombic phases.

**Table 5.** Static dielectric constant of CsPbI$_3$ for the cubic and orthorhombic phases.

| Perovskite Structures     | $\varepsilon_0$ |
|---------------------------|------------------|
| CsPbI$_3$—Cubic           | 7.58             |
| CsPbI$_3$—Orthorhombic    | 3.42             |
Absorption and refractive spectra were also calculated from the dielectric function for both structural phases of CsPbI$_3$ and represented in Figure 7. The values obtained for the wavelength of the absorption edge and refraction index are given in Table 6. As can be seen, the structural phase transition of pure inorganic CsPbI$_3$ perovskite causes a decrease in the absorption edge wavelength and also in the refractive index. The origin of these reductions in the optical parameters is the changes in the volume, distortion index, and bond angle variance of inorganic Pb-I octahedra, which affects the distribution of cesium cation interactions with the Pb-I framework.

![Figure 7.](image)

**Figure 7.** (a) Optical absorption spectrum (the absorption edges are shown by yellow circles), (b) Refraction spectrum of CsPbI$_3$ for the cubic and orthorhombic phases.

**Table 6.** Wavelength of absorption edge and refraction index of CsPbI$_3$ structure for the cubic and orthorhombic phases.

| Perovskite Structures         | $n_0$ | $a$ (nm) |
|-------------------------------|-------|----------|
| CsPbI$_3$ – Cubic             | 2.75  | 779      |
| CsPbI$_3$ – Orthorhombic      | 1.82  | 506      |

4. Conclusions

The present first-principles theoretical study of pure CsPbI$_3$ inorganic perovskite at two temperatures of 300 °C and 25 °C revealed that a change in the structure of Pb6 inorganic octahedra substantially influences the electronic properties of CsPbI$_3$. Lowering the temperature causes a change in the volume, distortion index, and bond angle variance of the PbI$_6$, which in turn changes the structural phase of the inorganic perovskite. The tilted inorganic octahedra with an increased volume gives rise to the Van der Waals interactions between the cesium cation and PbI$_6$ framework. This increases the band gap value and causes a blue shift in the wavelength of absorption edge. Investigation of the effect of temperature change on the structural, electronic, and optical properties of hybrid inorganic perovskite is essential for a better understanding of these unrivaled materials.

**Author Contributions:** Conceptualization, R.S. and D.R.; methodology, M.K.M.N.; software, S.M.N.; validation, A.D. and M.D.A.; formal analysis, R.S.; investigation, D.R.; resources, M.K.M.N.; data curation, Q.W.; writing—original draft preparation, M.O.; writing—review and editing, A.D.; visualization, M.O.; supervision, A.D.; project administration, D.R.; funding acquisition, R.S. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.
Acknowledgments: This work was funded by the Researchers Supporting Project Number (RSP-2021/267) King Saud University, Riyadh, Saudi Arabia.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Zhou, Z.; Qin, J.; Xiang, X.; Tan, Y.; Liu, Q.; Xiong, N.N. News text topic clustering optimized method based on TF-IDF algorithm on spark. Comput. Mater. Contin. 2020, 62, 217–231. [CrossRef]
2. Tian, L.; Li, J.; Zhang, L.; Sun, Y.; Yang, S. TCPW BR: A wireless congestion control scheme base on RTT. Comput. Mater. Contin. 2020, 62, 233–244. [CrossRef]
3. Huang, Z.; Nie, Y.; Li, Y.; Ma, B.; Dui, G.; Yang, S.; Xin, L. Microstructural modeling and multiscale mechanical properties analysis of cancellous bone. Comput. Mater. Contin. 2020, 62, 245–265. [CrossRef]
4. Chen, H.; Heidari, A.A.; Chen, H.; Wang, M.; Pan, Z.; Gandomi, A.H. Multi-population differential evolution-assisted Harris hawks optimization: Framework and case studies. Futur. Gener. Comput. Syst. 2020, 111, 175–198. [CrossRef]
5. Wang, M.; Chen, H. Chaotic multi-swarm whale optimizer boosted support vector machine for medical diagnosis. Appl. Soft Comput. 2020, 88, 105946. [CrossRef]
6. Xu, Y.; Chen, H.; Luo, J.; Zhang, Q.; Jiao, S.; Zhang, X. Enhanced Moth-flame optimizer with mutation strategy for global optimization. Inf. Sci. 2019, 492, 181–203. [CrossRef]
7. Lee, B.; Lee, Y. Distinction between real faces and photos by analysis of face data. Intell. Autom. Soft Comput. 2020, 26, 133–139. [CrossRef]
8. Kim, M.; Kim, J.; Shin, M. Word embedding based knowledge representation with extracting relationship between scientific terminologies. Intell. Autom. Soft Comput. 2020, 26, 141–147. [CrossRef]
9. Park, J.-S.; Kim, S.-H. Noise cancellation based on voice activity detection using spectral variation for speech recognition in smart home devices. Intell. Autom. Soft Comput. 2020, 26, 149–159. [CrossRef]
10. Deng, J.; Chen, J.; Wang, D. Mechanism design and mechanical analysis of multi-suction sliding cleaning robot used in glass curtain wall. Comput. Syst. Sci. Eng. 2019, 34, 201–206. [CrossRef]
11. Nie, X.; Zou, X.; Zhu, D. Modeling and Simulation of entrepreneur individual based on dynamic and complex system computing. Comput. Syst. Sci. Eng. 2019, 34, 207–214. [CrossRef]
12. Hua, R.; Bao, Y.; Chen, S.; Zhuang, Z. Optimization of the dynamic measure of spillover effect based on knowledge graph. Comput. Syst. Sci. Eng. 2019, 34, 215–223. [CrossRef]
13. Yang, Z.; Surrente, A.; Galkowski, K.; Miyata, A.; Portugall, O.; Sutton, R.; Haghhighrad, A.; Snaith, H.; Maude, D.; Plochocka, P. Impact of the halide cage on the electronic properties of fully inorganic cesium lead halide perovskites. ACS Energy Lett. 2017, 2, 1621–1627. [CrossRef]
14. Hu, Y.; Bai, F.; Liu, X.; Ji, Q.; Miao, X.; Qiu, T.; Zhang, X. Bismuth incorporation stabilized α-CsPbI₃ for fully inorganic perovskite solar cells. ACS Energy Lett. 2017, 2, 2219–2227. [CrossRef]
15. Nam, J.K.; Chai, S.U.; Cha, W.; Choi, Y.J.; Kim, W.; Jung, M.S.; Kwon, J.; Kim, D.; Park, J.H. Potassium incorporation for enhanced performance and stability of fully inorganic lead halide perovskite solar cells. Nano Lett. 2017, 17, 2028–2033. [CrossRef]
16. Zhao, X.; Zhang, X.; Cai, Z.; Tian, X.; Wang, X.; Huang, Y.; Chen, H.; Hu, L. Chaos enhanced grey wolf optimization wrapped ELM for diagnosis of paraquat-poisoned patients. Comput. Biol. Chem. 2019, 78, 481–490. [CrossRef]
17. Li, C.; Hou, L.; Sharma, B.Y.; Li, H.; Chen, C.; Li, Y.; Zhao, X.; Huang, H.; Cai, Z.; Chen, H. Developing a new intelligent system for the diagnosis of tuberculous pleural effusion. Comput. Methods Programs Biomed. 2018, 153, 211–225. [CrossRef]
18. Wang, M.; Chen, H.; Yang, B.; Zhao, X.; Hu, L.; Cai, Z.; Huang, H.; Tong, C. Toward an optimal kernel extreme learning machine using a chaotic moth-flame optimization strategy with applications in medical diagnoses. Neurocomputing 2017, 267, 69–84. [CrossRef]
19. Bansal, S.; Chiu, M. Atmospherically processed and stable Cs-Pb based perovskite solar cells. MRS Adv. 2017, 2, 3083–3090. [CrossRef]
20. Davarpanah, A.; Shirmohammadi, R.; Mirshekari, B.; Aslani, A. Analysis of hydraulic fracturing techniques: Hybrid fuzzy approaches. Arab. J. Geosci. 2019, 12, 1–8. [CrossRef]
21. Swarnkar, A.; Marshall, A.R.; Sanehira, E.M.; Chermomordik, B.D.; Moore, D.T.; Christians, J.A.; Chakrabarti, T.; Luther, J.M. Quantum dot-induced phase stabilization of α-CsPbI₃ perovskite for high-efficiency photovoltaics. Science 2016, 354, 92–95. [CrossRef]
22. Duan, M.; Li, K.; Ouyang, A.; Win, K.N.; Li, K.; Tian, Q. EGroupNet: A feature-enhanced Network for age estimation with novel age group schemes. ACM Trans. Multim. Comput. Commun. Appl. 2020, 16, 1–23. [CrossRef]
23. Yang, W.; Li, K.; Li, K. A pipeline computing method of SpTV for three-order tensors on CPU and GPU. ACM Trans. Knowl. Discov. Data 2019, 13, 1–27. [CrossRef]
24. Zhou, X.; Li, K.; Yang, Z.; Xiao, G.; Li, K. Progressive approaches for pareto optimal groups computation. IEEE Trans. Knowl. Data Eng. 2019, 31, 521–534. [CrossRef]
25. Jing, M.; Li, K.; Tong, Z.; Li, Q.; Li, K. Profit maximization for cloud brokers in cloud computing. IEEE Trans. Parallel Distrib. Syst. 2019, 30, 190–203.
53. Tang, Q.; Wang, K.; Song, Y.; Li, F.; Park, J.H. Waiting time minimized charging and discharging strategy based on mobile edge computing supported by software-defined Network. *IEEE Internet Things J.* 2019, 7, 6088–6101. [CrossRef]

54. Zhang, J.; Yang, K.; Xiang, L.; Luo, Y.; Xiong, B.; Tang, Q. A self-adaptive regression-based multivariate data compression scheme with error bound in wireless sensor Networks. *Int. J. Distrib. Sens. Netw.* 2015, 9, 913497. [CrossRef]

55. Møller, C.K. Crystal structure and conductopitivity of caesium plumbohalide. *Nature* 1958, 182, 1436. [CrossRef]

56. Filip, M.R.; Verdi, C.; Giustino, F. GW band structures and carrier effective masses of CH$_3$NH$_3$PbI$_3$ and hypothetical perovskites of the type A$_n$Pb$_x$Cl$_{3-x}$ with A= NH$_3$, PbH$_2$, AsH$_3$, and SbH$_3$. *J. Phys. Chem. C.* 2015, 119, 25209–25219. [CrossRef]

57. Davies, C.L.; Filip, M.R.; Patel, J.B.; Crothers, T.W.; Verdi, C.; Wright, A.D.; Milot, R.L.; Giustino, F.; Johnston, M.B.; Herz, L.M. Bimolecular recombination in methylammonium lead triiodide perovskite is an inverse absorption process. *Nat. Commun.* 2018, 9, 1–9. [CrossRef]

58. Filip, M.R.; Eperon, G.E.; Snaith, H.J.; Giustino, F. Steric engineering of metal-halide perovskites with tunable optical band gaps. *Nat. Commun.* 2014, 5, 1–9. [CrossRef][PubMed]

59. Zhang, J.; Sun, J.; Wang, J.; Yue, X.-G. Visual object tracking based on residual network and cascaded correlation filters. *J. Ambient. Intell. Humaniz. Comput.* 2020, 12, 1–14. [CrossRef]

60. Zhao, D.; Liu, R.; Heidari, A.A.; Wang, X.; Chen, Y.; Wang, M.; Chen, H. Towards augmented kernel extreme learning models for bankruptcy prediction: Algorithmic learning and comprehensive analysis. *Neurocomputing* 2020, 430, 185–212. [CrossRef]

61. Zhao, D.; Liu, L.; Yu, F.; Heidari, A.A.; Wang, M.; Liang, G.; Muhammad, K.; Chen, H. Chaotic random sparse ant colony optimization for multi-threshold image segmentation of 2D Kapur entropy. *Knowl.-Based Syst.* 2020, 216, 106510. [CrossRef]

62. Tu, J.; Chen, H.; Liu, J.; Heidari, A.A.; Zhang, X.; Wang, M.; Ruby, R.; Pham, Q.-V. Evolutionary biogeography-based whale optimization methods with communication structure: Towards measuring the balance. *Knowl.-Based Syst.* 2020, 212, 106642. [CrossRef]

63. Gu, K.; Wang, Y.; Wen, S. Traceable threshold proxy signature. *J. Inf. Sci. Eng.* 2017, 33, 63–79.

64. Li, W.; Ding, Y.; Yang, Y.; Sherratt, R.S.; Park, J.H.; Wang, J. Parameterized algorithms of fundamental NP-hard problems: A survey. *Hum.-Cent. Comput. Inf. Sci.* 2020, 10, 1–24. [CrossRef]

65. Gu, K.; Yang, L.; Wang, Y.; Wen, S. Traceable identity-based group signature. *RAIRO-Theor. Inform. Appl.* 2016, 50, 193–226. [CrossRef]

66. Yin, B.; Zhou, S.; Lin, Y.; Liu, Y.; Hu, Y. Efficient distributed skyline computation using dependency-based data partitioning. *J. Syst. Softw.* 2014, 93, 69–83. [CrossRef]

67. Long, M.; Xia, X. Outage performance of double-relay cooperative transmission network with energy harvesting. *Phys. Commun.* 2018, 29, 261–267. [CrossRef]

68. Xu, Z.; Liang, W.; Li, K.-C.; Xu, J.; Jin, H. A blockchain-based Roadside Unit-assisted authentication and key agreement protocol for Internet of Vehicles. *J. Parallel Distrib. Comput.* 2021, 149, 29–39. [CrossRef]

69. Wang, W.; Yang, Y.; Li, J.; Hu, Y.; Luo, Y.; Wang, X. Woodland labeling in chenzhou, China, via deep learning approach. *Int. J. Comput. Intell. Syst.* 2020, 13, 1393–1403. [CrossRef]

70. Ehyaei, M.A.; Ahmadi, A.; Rosen, M.A.; Davarpanah, A. Thermodynamic optimization of a geothermal power plant with a genetic algorithm in two stages. *Processes* 2020, 8, 1277. [CrossRef]

71. Stoumpos, C.C.; Kanatzidis, M.G. The renaissance of halide perovskites and their evolution as emerging semiconductors. *Acc. Chem. Res.* 2015, 48, 2791–2802. [CrossRef][PubMed]

72. Marronnier, A.; Roma, G.; Boyer-Richard, S.; Pedesseau, L.; Jancu, J.-M.; Bonnassieux, Y.; Katan, C.; Stoumpos, C.C.; Kanatzidis, M.G.; Even, J. Anharmonicity and disorder in the black phases of cesium lead iodide used for stable inorganic perovskite solar cells. *ACS Nano* 2018, 12, 3477–3486. [CrossRef]

73. Hu, X.; Xie, J.; Cai, W.; Wang, R.; Davarpanah, A. Thermodynamic effects of cycling carbon dioxide injectivity in shale reservoirs. *J. Pet. Sci. Eng.* 2020, 195, 107717. [CrossRef]

74. Davarpanah, A.; Mirshakari, B. Experimental investigation and mathematical modeling of gas diffusivity by carbon dioxide and methane kinetic adsorption. *Ind. Eng. Chem. Res.* 2019, 58, 12392–12400. [CrossRef]

75. Fu, Y.; Zhu, H.; Stoumpos, C.C.; Ding, Q.; Wang, J.; Kanatzidis, M.G.; Zhu, X.; Jin, S. Broad wavelength tunable robust lasing from single-crystal nanowires of cesium lead halide perovskites (CsPbX$_3$, X= Cl, Br, I). *ACS Nano* 2016, 10, 7963–7972. [CrossRef]

76. Shan, W.; Qiao, Z.; Heidari, A.A.; Chen, H.; Turabieh, H.; Teng, Y. Double adaptive weights for stabilization of moth flame optimizer: Balance analysis, engineering cases, and medical diagnosis. *Knowl.-Based Syst.* 2014, 216, 106510. [CrossRef]

77. Yu, C.; Chen, M.; Cheng, K.; Zhao, X.; Ma, C.; Kuang, F.; Chen, H. SGOA: Annealing-behaved grasshopper optimizer for global tasks. *Eng. Comput.* 2021, 1–28. [CrossRef]

78. Hu, J.; Chen, H.; Heidari, A.A.; Wang, M.; Zhang, X.; Chen, Y.; Pan, Z. Orthogonal learning covariance matrix for defects of grey wolf optimizer: Insights, balance, diversity, and feature selection. *Knowledge-Based Syst.* 2021, 213, 106684. [CrossRef]

79. Zhao, X.; Li, D.; Yang, B.; Ma, C.; Zhu, Y.; Chen, H. Feature selection based on improved ant colony optimization for online detection of foreign fiber in cotton. *Appl. Soft Comput.* 2014, 24, 585–596. [CrossRef]

80. Yu, H.; Li, W.; Chen, C.; Liang, J.; Gui, W.; Wang, M.; Chen, H. Dynamic Gaussian bare-bones fruit fly optimizers with abandonment mechanism: Method and analysis. *Eng. Comput.* 2020, 1–29. [CrossRef]
81. Frolova, L.A.; Anokhin, D.V.; Piryazev, A.A.; Luchkin, S.Y.; Dremova, N.N.; Stevenson, K.J.; Troshin, P.A. Highly efficient all-inorganic planar heterojunction perovskite solar cells produced by thermal coevaporation of CsI and PbI2. J. Phys. Chem. Lett. 2017, 8, 67–72. [CrossRef]

82. Lai, M.; Kong, Q.; Bischak, C.G.; Yu, Y.; Dou, L.; Eaton, S.W.; Ginsberg, N.S.; Yang, P. Structural, optical, and electrical properties of phase-controlled cesium lead iodide nanowires. Nano Res. 2017, 10, 1107–1114. [CrossRef]

83. Paul, T.; Chatterjee, B.; Maiti, S.; Sarkar, S.; Besra, N.; Das, B.; Panigrahi, K.; Thakur, S.; Ghorai, U.; Chattopadhyay, K. Tunable cathodoluminescence over the entire visible window from all-inorganic perovskite CsPbBr3 1D architecture. J. Mater. Chem. C 2018, 6, 3322–3333. [CrossRef]

84. Fu, Y.; Rea, M.T.; Chen, J.; Morrow, D.J.; Hautzinger, M.P.; Zhao, Y.; Pan, D.; Manger, L.H.; Wright, J.C.; Goldsmith, R.H. Selective stabilization and photophysical properties of metastable perovskite polymorphs of CsPbI3 in thin films. Chem. Mater. 2017, 29, 8385–8394. [CrossRef]

85. Bertolotti, F.; Protesescu, L.; Kovalenko, M.V.; Yakunin, S.; Billinge, S.J.; Terban, M.; Pedersen, J.P.; Masciocchi, N.; Guagliardi, A. Coherent nanotwins and dynamic disorder in cesium lead halide perovskite nanocrystals. ACS Nano 2017, 11, 3819–3831. [CrossRef]

86. Hybertsen, M.S.; Louie, S.G. Electron correlation in semiconductors and insulators: Band gaps and particle energies. Phys. Rev. B 1986, 34, 5390. [CrossRef][PubMed]

87. Linaburg, M.R.; McClure, E.T.; Majher, J.D.; Woodward, P.M. Cs1-xRbxBaCl3 and Cs1-xRbxBaBr3 solid solutions: Understanding octahedral tilting in lead halide perovskites. Chem. Mater. 2017, 29, 3507–3514. [CrossRef]

88. Yamada, K.; Funabiki, S.; Horimoto, H.; Matsui, T.; Okuda, T.; Ichiba, S. Structural phase transitions of the polymorphs of CsSnI3 by means of rietveld analysis of the X-ray diffraction. Chem. Lett. 1991, 20, 801–804. [CrossRef]

89. Chung, I.; Song, J.-H.; Androulakis, J.; Malliakas, C.D.; Li, H.; Freeman, A.J.; Kenney, J.T.; Kanatzidis, M.G. CsSnI3: Semiconductor or metal? High electrical conductivity and strong near-infrared photoluminescence from a single material. High hole mobility and phase-transitions. J. Am. Chem. Soc. 2012, 134, 8579–8587. [CrossRef]

90. Hutter, E.M.; Sutton, R.J.; Chandrashekar, S.; Abdi-Jalebi, M.; Stranks, S.D.; Snaith, H.J.; Savenije, T.J. Vapour-deposited cesium lead iodide perovskites: Microsecond charge carrier lifetimes and dynamic disorder in cesium lead halide perovskite nanocrystals. ACS Energy Lett. 2017, 2, 1901–1908. [CrossRef]

91. Shahiduzzaman, M.; Yonezawa, K.; Yamamoto, K.; Ripolles, T.S.; Karakawa, M.; Kuwabara, T.; Takahashi, K.; Hayase, T.; Taima, T. Improved reproducibility and intercalation control of efficient planar inorganic perovskite solar cells by simple alternate vacuum deposition of PbI2 and CsI. ACS Omega 2017, 2, 4464–4469. [CrossRef]

92. Yang, L.; Dai, Q.; Liu, L.; Shao, D.; Luo, K.; Jamil, S.; Liu, H.; Luo, Z.; Chang, B.; Wang, X. Rapid sintering method for highly conductive Li+La3Zr2O12 ceramic electrolyte. Ceram. Int. 2020, 46, 10917–10924. [CrossRef]

93. Li, X.; Feng, Y.; Liu, B.; Yi, D.; Yang, X.; Zhang, W.; Chen, G.; Liu, Y.; Bai, P. Influence of NbC particles on microstructure and mechanical properties of AlCoCrFeNi high-entropy alloy coatings prepared by laser cladding. J. Alloy. Compd. 2021, 416, 125738. [CrossRef][PubMed]

94. Chen, X.; Wang, W.; Wang, T.; Yang, Z.; Zou, X.; Wang, P.; Luo, W.; Li, Q.; Liao, L.; Hu, W. Enhanced photocurrent sensitivity of a GaAs nanowire metal-semiconductor-metal photodetector by adjusting the Fermi level. ACS Appl. Interfaces 2019, 11, 33188–33193. [CrossRef][PubMed]

95. Li, H.; Tang, J.; Kang, Y.; Zhao, H.; Fang, D.; Fang, X.; Chen, R.; Wei, Z. Optical properties of quasi-type-II structure in GaAs/GaAsSb/GaAs coaxial single quantum-well nanowires. Appl. Phys. Lett. 2018, 113, 233104. [CrossRef]

96. Zhang, T.; Wu, X.; Shaheen, S.M.; Rinklebe, J.; Bolan, N.S.; Ali, E.F.; Li, G.; Tsang, D.C. Effects of microorganism-mediated inoculants on humification processes and phosphorus dynamics during the aerobic composting of swine manure. Appl. Phys. Lett. 2018, 1104–1113. [CrossRef]

97. Wang, M.; Jiang, C.; Zhang, S.; Song, X.; Tang, Y.; Cheng, H.-M. Reversible calcium alloying enables a practical room-temperature rechargeable calcium-ion battery with a high discharge voltage. Nat. Chem. 2018, 10, 667–672. [CrossRef]

98. Li, X.; Sheng, X.; Guo, Y.; Lu, X.; Wu, H.; Chen, Y.; Zhang, L.; Gu, J. Multifunctional HDPE/CNTs/PW composite phase change materials with excellent thermal and electrical conductivities. J. Mater. Sci. Technol. 2021, 86, 171–179. [CrossRef]

99. Niu, Z.; Zhang, B.; Li, D.; Ji, D.; Liu, Y.; Feng, Y.; Zhou, T.; Zhang, Y.; Fan, Y.; Niu, A.Z. A mechanical reliability study of 3-dB waveguide hybrid couplers in submillimeter and terahertz bands. Front. Inf. Technol. Electron. Eng. 2021, 22, 1104–1113. [CrossRef]

100. Woodward, P.M. Octahedral tilting in perovskites. I. Geometrical considerations. Acta Crystallogr. Sect. B Struct. Sci. 1997, 53, 44–66. [CrossRef]

101. Woodward, P.M. Octahedral tilting in perovskites. II. Structure stabilizing forces. Acta Crystallogr. Sect. B Struct. Sci. 1997, 53, 32–43. [CrossRef]

102. Glazer, A.M. The classification of tilted octahedra in perovskites. Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem. 1972, 28, 3384–3392. [CrossRef]
105. Nam, J.K.; Jung, M.S.; Chai, S.U.; Choi, Y.J.; Kim, D.; Park, J.H. Unveiling the crystal formation of cesium lead mixed-halide perovskites for efficient and stable solar cells. *J. Phys. Chem. Lett.* **2017**, *8*, 2936–2940. [CrossRef] [PubMed]

106. Ripolles, T.S.; Nishinaka, K.; Ogomi, Y.; Miyata, Y.; Hayase, S. Efficiency enhancement by changing perovskite crystal phase and adding a charge extraction interlayer in organic amine free-perovskite solar cells based on cesium. *Sol. Energy Mater. Sol. Cells* **2016**, *144*, 532–536. [CrossRef]

107. Luo, P.; Xia, W.; Zhou, S.; Sun, L.; Cheng, J.; Xu, C.; Lu, Y. Solvent engineering for ambient-air-processed, phase-stable CsPbI3 in perovskite solar cells. *J. Phys. Chem. Lett.* **2016**, *8*, 3603–3608. [CrossRef]

108. Li, H.; Xu, P.; Liu, D.; He, J.; Zu, H.; Song, J.; Zhang, J.; Tian, F.; Yun, M.; Wang, F. Low-voltage and fast-response SnO2 nanotubes/perovskite heterostructure photodetector. *Nanotechnology* **2021**, *32*, 375202. [CrossRef]

109. Li, F.; Ma, C.; Wang, H.; Hu, W.; Yu, W.; Sheikh, A.D.; Wu, T. Ambipolar solution-processed hybrid perovskite phototransistors. *Nat. Commun.* **2015**, *6*, 1–8. [CrossRef]

110. Eperon, G.E.; Stranks, S.D.; Menelaou, C.; Johnston, M.B.; Herz, L.M.; Snaith, H.J. Formamidinium lead trihalide: A broadly tunable perovskite for efficient planar heterojunction solar cells. *Energy Environ. Sci.* **2014**, *7*, 982–988. [CrossRef]

111. Swarnkar, A.; Chulliyil, R.; Ravi, V.K.; Irfanullah, M.; Chowdhury, A.; Nag, A. Colloidal CsPbBr3 perovskite nanocrystals: Luminescence beyond traditional quantum dots. *Angew. Chem.* **2015**, *127*, 15644–15648. [CrossRef]

112. Zarei, M.; Davarpanah, A.; Mokhtarian, N.; Farahbod, F. Integrated feasibility experimental investigation of hydrodynamic, geometrical and, operational characterization of methanol conversion to formaldehyde. *Energy Sources Part A Recovery Util. Environ. Eff.* **2020**, *42*, 89–103. [CrossRef]

113. Ananthakumar, S.; Kumar, J.R.; Babu, S.M. Cesium lead halide (CsPbX₃, X= Cl, Br, I) perovskite quantum dots-synthesis, properties, and applications: A review of their present status. *J. Photonics Energy* **2016**, *6*, 042001. [CrossRef]

114. Tang, X.; Hu, Z.; Chen, W.; Xing, X.; Zang, Z.; Hu, W.; Qiu, J.; Du, J.; Leng, Y.; Jiang, X. Room temperature single-photon emission and lasing for all-inorganic colloidal perovskite quantum dots. *Nano Energy* **2016**, *28*, 462–468. [CrossRef]

115. Somma, F.; Nikl, M.; Nitsch, K.; Fabeni, P.; Pazzi, G. Excitons in CsPbI₃ (X= Cl, Br, I) ternary nanocrystallites in thin film matrices. *J. Lumin.* **2001**, *94*, 169–172. [CrossRef]

116. Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G.L.; Cococcioni, M.; Dabo, I. QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials. *J. Phys. Condens. Matter* **2009**, *21*, 395502. [CrossRef] [PubMed]

117. Perdew, J.P.; Zunger, A. Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B* **1981**, *23*, 5048. [CrossRef]

118. Monkhorst, H.J.; Pack, J.D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, *13*, 5188. [CrossRef]

119. Pack, J.D.; Monkhorst, H.J. “Special points for Brillouin-zone integrations”—A reply. *Phys. Rev. B* **1977**, *16*, 1748. [CrossRef]