Perspective

From tetragonal to cubic: perovskite phase structure evolution for high-performance solar cells

Qi Wei [a,b,1], Hao Liang [a,1], Yuki Haruta [c], Makhsud Saidaminov [c], Qixi Mi [a], Michael Saliba [d], Guanglei Cui [e], Zhijun Ning [a,*]

[a] School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China
[b] High Performance Computing Department, National Supercomputing Center in Shenzhen, Shenzhen 200441, China
[c] Department of Chemistry and Department of Electrical & Computer Engineering and Centre for Advanced Materials and Related Technologies (CAMTEC), University of Victoria, Victoria V8P 5C2, Canada
[d] Institute for Photovoltaics, University of Stuttgart, Stuttgart 70569, Germany
[e] Qingdao Industrial Energy Storage Research Institute, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China

Crystal structure, which is generally determined by the composition, ionic radius and valence state of constituent elements, plays a significant role in the material's fundamental properties such as optical, electronic, and mechanical characters. The manipulation of the crystal structure through compositional engineering, and understanding the relationship between crystal structure and properties are essential for the development of materials.

The past decade has witnessed the significant development of halide perovskites, especially in the field of solar cells, owing to their suitable bandgap and outstanding electronic and optical properties. Halide perovskite typically has an ABX_3 structure, in which the A-site is a cation of +1 state, B-site +2 cation, and X-site halide. Compositional engineering has arguably played a key role to enhance the performance of perovskite solar cells. Methylammonium (MA) was initially used as the A-site cation, and it is now partially or fully replaced by the large formamidinium (FA) molecule due to its relative thermal stability and beneficially red-shifted bandgap allowing for an improved theoretical limit [1,2]. Thus, FA-dominant perovskites significantly prompted the efficiency of perovskite solar cells, now reaching 25.7%.

Meanwhile, perovskites with different structures such as cubic, tetragonal, and orthorhombic phases have been reported. However, their role in device performance is generally underexplored. Here, we briefly summarize the phase structure of perovskite and the construction of perovskite phases by compositional engineering. Subsequently, the relationship between the perovskite phase structure and its properties such as carrier transport, electronic structure, stability, and carrier lifetime is discussed, and the advantages of cubic phase perovskite are emphasized.

Phase structure of perovskites. Perovskites with the chemical formula of ABX_3 undergo several temperature-dependent phase transitions, corresponding mostly to rotation and distortion of the $[BX_6]^{4-}$ octahedra. Generally, at a high temperature, the material maintains a highly symmetric cubic structure (α-phase); as the temperature decreases, the cubic structure is distorted and the crystal symmetry is lowered, resulting in the phase transition to tetragonal, orthorhombic, or even hexagonal structure [3]. Experimentally, there is also a cursory phase category for perovskites: the black phase (e.g., cubic structure) and the yellow phase (e.g., hexagonal structure), which can be visibly distinguished by their color due to the distinct bandgap difference. The black phase is needed for perovskite solar cells since the yellow phase is not photoactive due to its limited absorption range.

Table 1 offers a summary of the phase structure for some common perovskites. Apart from the temperature, changes in ionic radius can modify the tolerance factor leading to a change in the perovskite phase structure. For example, the pure $MAPbI_3$ generally exhibits a tetragonal structure at room temperature as the A-site cations are not sufficiently large to fill up the empty voids between the $[PbI_6]^{4-}$ octahedral structures. While $MAPbI_3$ still keeps the corner-shared octahedral framework, cubic $FAPbI_3$ (α-phase) can turn into a hexagonal phase (δ-phase) at room temperature where the framework is broken since the FA^+ ions are too large. For $CsPbI_3$, on the contrary, the Cs^+ ions are too small to fill the corner-sharing octahedral framework at room temperature, although $CsPbI_3$ can turn into a black phase at high temperatures [4]. Meanwhile, the larger X-site ions can effectively reduce the binding between Pb, and we can use the tolerance factor to describe its influence on the crystal structure [5].

Here, we focus on the cubic and tetragonal structure of the black phase, which can be obtained at room temperature and are widely used for solar cells. As shown in Fig. 1, apart from pure perovskites, mixing cations or halogens is another way to form the cubic structure. This not only increases the configuration entropy but also regulates the tolerance factor [6]. Many oversized cations like methylenediammonium (MDA^+), dimethylammonium (DMA^+), ethylammonium (EA^+), guanidinium (Gua^+) and undersized cations like Cs^+, Rb^+, K^+ are introduced to balance the volume space for the formation of the compact cubic phase structure [7,8]. Shi et al. [9] proposed a volume-based criterion of $V/Z = 252 \pm 3$ $Å^3$ for the for-

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* Corresponding author.
  E-mail address: ningzhj@shanghaitech.edu.cn (Z. Ning).
[1] These authors contributed equally to this work.

Table 1
Different phase structures of perovskites.

Perovskite	Phase	Space group	Temperature (K)[a]
MAPbI$_3$	Cubic (α-phase)	$Pm\bar{3}m$	>330
	Tetragonal (β-phase)	$I4/mcm$	160–330
	Orthorhombic (γ-phase)	$Pnma$	<160
FAPbI$_3$	Cubic (α-phase)	$Pm\bar{3}m$	390
	Trigonal (pesudo-cubic)	$P3m1$	373
	Hexagonal (δ-phase)	$P6_3/mmc$	220
CsPbI$_3$	Cubic (α-phase)	$Pm\bar{3}m$	573
	Tetragonal (β-phase)	$P4/mbm$	510
	Orthorhombic (γ-phase)	$Pbnm$	325
	Orthorhombic (δ-phase)	$Pnma$	298
MASnI$_3$	Cubic (α-phase)	$Pm\bar{3}m$	296
	Orthorhombic (β-phase)	$Imm2$	180
FASnI$_3$	Cubic (α-phase)	$Pm\bar{3}m$	296
	Tetragonal (β-phase)	$I4cm$	200
	Hexagonal (δ-phase)	$P6_3cm$	293
CsSnI$_3$	Cubic (α-phase)	$Pm\bar{3}m$	500
	Tetragonal (β-phase)	$P4/mbm$	380
	Orthorhombic (γ-phase)	$Pnma$	300

[a] The temperature of MAPbI$_3$ refers to the range in which different phases exist. Other temperatures indicate the presence of this phase at this temperature.

mation of stable cubic APbI$_3$ perovskite, where, V/Z represents volume per formula unit. For FA-based perovskite, the introduction of small-sized A-site cations including Rb$^+$, Cs$^+$, and MA$^+$ has been reported to increase the entropy to improve stability. Meanwhile, MDA$^+$ with a similar ion radius as FA$^+$ is also reported to facilitate the formation of the cubic phase due to the presence of more H atoms forming hydrogen bonds with the I atoms. For MA-based perovskite, larger cations are introduced including DMA$^+$, EA$^+$, and Gua$^+$ to form a cubic phase. Besides A-site mixing, the modulation of X-site ions is another way to form a cubic structure. It is reported that the tetragonal phase of MAPbI$_3$ turns to a cubic phase when the ratio of Br is ~0.2 [10], and thus the doping of Br is widely observed in high-performance perovskite solar cells. Noticeably, for both pure and mixed perovskite, the organic molecules in the cubic phase are generally thought to be dynamically disordered to achieve high symmetry on average; as a result, they are also called to be in the pseudo-cubic phase.

Optoelectronic and thermal properties. Phase structure plays an important role in the optical and electronic properties of perovskites. Firstly, the bandgap of perovskite is affected by the phase structure due to the different orbital overlaps with the $[BX_6]^{4-}$ framework. For instance, the bandgaps for MAPbI$_3$ with different phase structures show ~0.1 eV difference. Cubic phase FA-dominant structure generally offers a lower bandgap as its larger ion radius can provide better orbital overlap with the $[BX_6]^{4-}$ framework. Theoretical calculations confirm that the cubic phase structure possesses a narrower bandgap due to the stronger electron coupling compared to the structure with a tilted $[BX_6]^{4-}$ octahedra [11].

The phase variation also changes the defect formation energy of perovskites. A systematic structural rigidity comparison between the cubic phase DMA$_{0.125}$MA$_{0.875}$PbI$_3$ and the tetragonal phase MAPbI$_3$ was conducted by Chen and co-workers [12]. With adiabatic molecular dynamic simulations, the change in the average length of Pb–I bonds in DMA$_{0.125}$MA$_{0.875}$PbI$_3$ due to thermal expansion was found to be smaller than that of MAPbI$_3$. And decreased
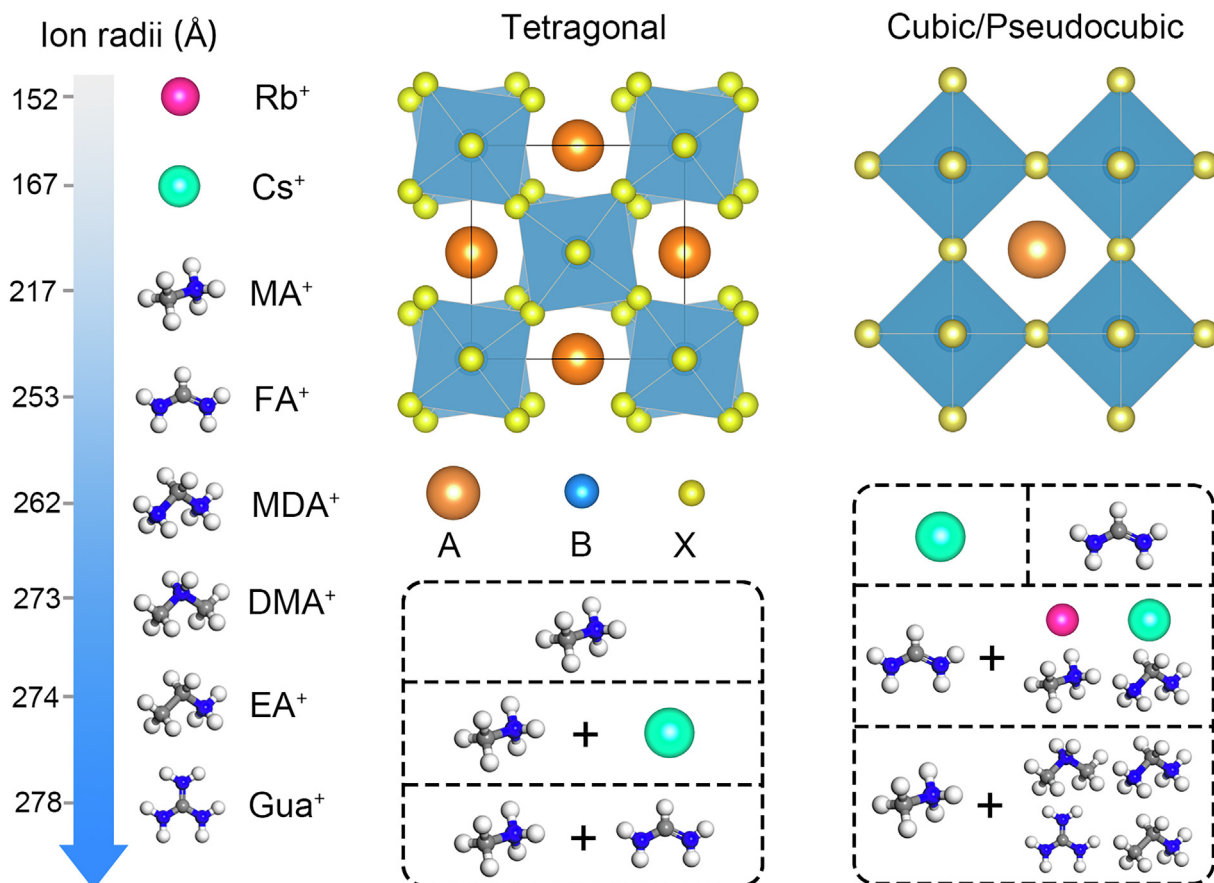

Fig. 1. The formation of tetragonal and cubic phase perovskite with different combinations of the A-site cations.

canonically averaged standard deviation of the position of I and Pb atoms is also observed in $DMA_{0.125}MA_{0.875}PbI_3$, indicating it is more rigid. Further calculations prove that the increased rigidity is responsible for the reduced defect density (Fig. 2a), reduced non-radiative recombination, and ion migration which are beneficial for the device performance.

The lattice dynamics are important for the development of quantitative models for the generation, transport, and recombination of photogenerated carriers in hybrid perovskite solar cells. The high degree of freedom of the organic cation and the soft $[BX_6]^{4-}$ framework of perovskites result in a shorter phonon lifetime compared to conventional semiconductors. And both theoretical and experimental studies found that the phonon lifetime decreases as the structure changes from orthorhombic to tetragonal, and to cubic [13,14]. The short phonon lifetimes can result in low thermal transport, and the hot carrier cooling is delayed as the inefficient acoustic phonon propagation will result in local heating, creating a nonequilibrium population of optical phonons that can effectively reheat carriers, leading to long hot carrier lifetimes [14]. This further reduces the nonradiative recombination of band edge carriers.

Besides, the cubic phase is reported to enhance the spin–orbit coupling (SOC) effect compared to the octahedral-tilted tetragonal phase due to the increased ionic character of Pb–I bonds. This then enhances the Pb character in the materials conduction, thus amplifying the effect of SOC [15]. Meanwhile, the disordered orientation of the molecules in cubic phase perovskite leads to a dynamic symmetry broken. The broken symmetry combined with the strong SOC induces Rashba effect that causes a momentum-dependent spin splitting of electronic bands. The Rashba splitting results in the formation of an indirect bandgap, which significantly reduces the radiative recombination rates. It is believed that the direct bandgap character in optical absorption and the indirect bandgap character in carrier recombination of perovskites are responsible for the high efficiencies achieved by perovskite solar cells [16]. In Fig. 2c, the carrier lifetime of the high-performance perovskite with tetragonal and cubic structures are plotted, which clearly indicates that the cubic structural perovskite presents a longer carrier lifetime even compared to some of the single crystals with tetragonal structures [16].

Material and device stability. Stability is another critical factor that needs to be improved to compete with commercial
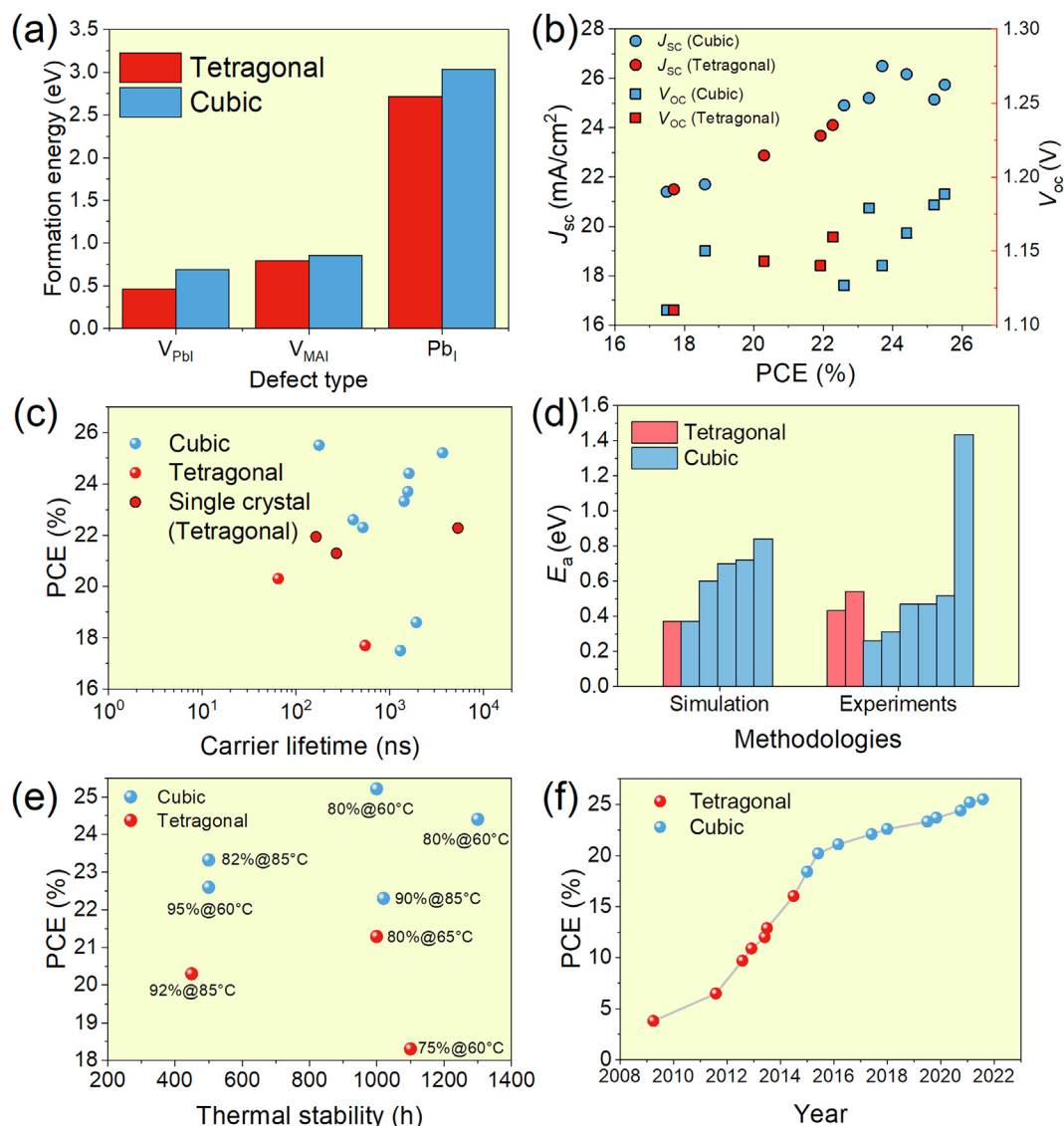

Fig. 2. Defect formation energy (a), V_{OC} and J_{SC} (b), carrier lifetime (c), activation energy of ion migration (d), thermal stability (e), and best efficiency chart of perovskite along the phase structure (f).

photovoltaic technologies. Theoretical simulations indicate that the cubic phase structure has enhanced rigidity in comparison to the tetragonal phase. We also proved it by micro area electrochemical measurement, in which cubic phase structure showed slower ion moving [12]. In an aqueous solution, the cubic phase structure shows enhanced stability than the tetragonal phase [9]. Fig. 2d shows that the cubic phase perovskites show higher activation energy for ion migration than that of tetragonal phase ones. This also explains the recent progress in the stability of perovskites. For the thermal stability, as shown in Fig. 2e, the cubic phase perovskites also show better thermal stability over 1300 h as well as higher efficiency.

Solar cell efficiency. The efficiency of perovskite solar cells increases quickly in recent years. The higher efficiency is derived from higher short circuit current and open circuit voltage. Due to the smaller bandgap of FA-dominant cubic structure, the light-harvesting range was extended to 850 nm for lead-based perovskite, higher than that with a tetragonal structure. Furthermore, the enhanced carrier lifetime and carrier mobility contributed to the enhanced carrier diffusion length. As a result, the current density was increased to 26.5 mA/cm^2, higher than that based on the tetragonal phase structure. On the other hand, despite the bandgap becoming smaller, the open circuit voltage was increased as well (1.19 V) [6] likely due to the reduced defect density of the perovskite materials. Apart from lead perovskites, the high-performing tin perovskite solar cells are also mainly based on FA-dominant cubic structures.

Conclusion and outlook. Overall, this perspective summarizes the interrelation between the phase structure and the composition of lead perovskites, and the influence of the phase structure on the properties and solar cell performance. The cubic phase shows desirable properties such as low defect density, long carrier lifetime, large wide absorbance range, and enhanced stability. These features facilitate the performance enhancement of perovskite solar cells. It can be expected that cubic phase structure will be more popular for perovskite solar cells, as well as other optoelectronic devices.

The advantages of cubic perovskite also provide some guidance for the future development of perovskite solar cells and optoelectronic devices, including the modulation of the interface band alignment with phase structure, the utilization of the Rashba splitting for spintronic devices, the manipulation of anion size, and theories to accurately predict the phase structure of perovskites (Fig. S1 online). In addition, despite the advantages of the cubic phase discussed above, some other drawbacks or underlying mechanisms of this structure remain to be investigated, such as the stabilization of the structure in competing with the δ-phase, phase transition after the doping, the seeming contradiction between the rigid structure and the soft lattice framework, as well as the bandgap difference between theoretical calculations and experimental measurements.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

Appendix A. Supplementary materials

Supplementary materials to this perspective can be found online at https://doi.org/10.1016/j.scib.2023.01.008.

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Qi Wei received her Ph.D. degree from ShanghaiTech University in 2022, under the supervision of Prof. Zhijun Ning. She received her Bachelor's degree (2017) in Energy and Power Engineering from East China University of Science and Technology. Her research focuses on first-principles calculations on optoelectronic materials.

Hao Liang is a graduate student at the School of Physical Science and Technology, ShanghaiTech University, under the supervision of Prof. Zhijun Ning. His research focuses on perovskite solar cells.

Zhijun Ning is a tenured associate professor at the School of Physical Science and Technology, ShanghaiTech University. He received his Ph.D. degree from the East China University of Science and Technology in 2009. From 2009 to 2014, he worked as a postdoctoral scholar fellow at the Royal Institute of Technology and the University of Toronto. He joined ShanghaiTech University in 2014. His group focuses on the development of solution-processed optoelectronic materials and devices.