

Review On Hybrid Organic-Inorganic Halide Perovskite

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Abstract: Hybrid organic-inorganic halide perovskite (HOIHP) is a new class of semi-conducting material which has proved to be a promising candidate for solar based devices. The efficiency of this perovskite material on harvesting solar energy has increased from 3% in 2006 to over 24% in 2019. The ability of HOIHP to absorb both visible and near-infrared light has made new research attempts towards the development of photodetectors, light emitting diodes, magneto-optic effects and scintillators. In contrast, silicon which has been in commercial use for many decades has reached a limiting point beyond which improvement of quantum efficiency has become drastically saturated. Moreover, unlike hybrid perovskite materials silicon for solar cell applications requires processing at high temperature. The additional advantages of HOIHP material are the high cross section for photo-electron generation and the long diffusion length of charge carriers.

Structure of Hybrid perovskite

Perovskite is a crystal structure with formulae ABX_3 which comes with large number of polymorphs that depends on various perturbation like temperature, pressure and electromagnetic field [1, 2]. The unit cell of perovskites comprises of 5 atoms in a cubic structure where cation A having coordination number 12 sits at the corners of the cube while BX_6 makes an octahedra environment where cation B shares with 6 anion X atoms. To maintain the highly symmetric cubic structure of perovskite the ionic radii of A, B and X atoms should satisfy tolerance factor "t" which is given as

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

where R denotes the ionic radii

of corresponding ions. For crystal structure to be stable t should be close to ≈ 1 otherwise the crystal will have lower symmetry with distorted structure. The Perovskite structure as shown in Fig. 1 indicates the ionic radii of A is much greater than B ion which is the requirement for t to be close to 1 [3].

The versatility of HOIHP perovskite materials lies to the fact that it can form multidimensional structures pertaining to the same structural ABX_3 formulae through use of different combinations of various elements [4]. As for example

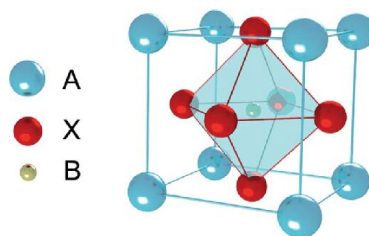


Figure 1: A perovskite structure with A site cation is at the center of the cell formed of corner sharing BX₆ octahedra.

BaTiO₃, CaTiO₃, BiFeO₃ are all well known perovskites where A and B sites are mainly occupied by inorganic ions. These inorganic perovskites are mainly characterized by covalent and ionic bonds which creates potential for high electrical mobility, varieties of band gaps ranging from insulators to superconductors, different flavors of magnetism and substantial mechanical and thermal stability.

A new room for scientific exploration and technical application opens up when a complex perovskite structure based on molecular scale composite of organic and inorganic cations is taken into consideration. In contrast to the inorganic perovskites organic molecules interact through weaker bondings like hydrogen and van der Waals interaction which leads to more structural diversity, large degree of polarizability, plasticity along with reduced weight and many other interesting optical properties [5]. For example if A cation has to be replaced by an organic molecule then the criteria of tolerance has still need to be fulfilled. If B cation is taken as Pb, and X anion is taken to be a halide say iodide, then $R_{Pb} + R_I = (1.19 + 2.20)$ Angstrom which means two or three atoms in a smallest organic molecule would fit well in the crystal structure because C-C or C-N bond lengths are of order 1.4 Angstrom. Methylammonium (CH₃NH₃)⁺ cation is found to be a good organic candidate for a perovskite structure which is shown in Fig.2.

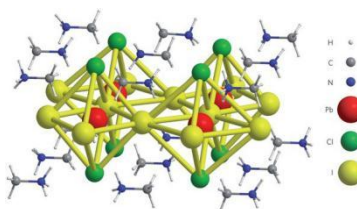


Figure 2: A hybrid perovskite structure with an organic cation (CH₃NH₃⁺) at A site is corner shared by PbI₆ octahedra.

So far many organic-inorganic hybrid perovskites like $\text{CH}_3\text{NH}_3\text{MX}_3$, where $\text{M} = \text{Sn}, \text{Pb}$ and $\text{X} = \text{Cl}, \text{Br}$ and Iodine of different lattice constants have been synthesized successfully. Other developments like tuning hybrid perovskite properties with chemical compositions as in case of mixed halide system ($\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$) has also been reported with better optimizing qualities. Electronic structure of perovskite

Perovskite is considered to be a multi functional material as because a broad spectrum of atoms can be incorporated each with different valency so long as charge neutrality is maintained. Band structure and density of states of perovskites are studied widely to know about the transport properties of this materials particularly $\text{CH}_3\text{NH}_3\text{PbI}_3$. Using DFT calculations, Pb shows occupied 6s orbital lies below the top of valence bands of perovskites [6]. This lone pair (inert node) of s electron in Pb often tends to show unusual properties. Density of states (DOS) also shows valence band maximum (VBM) has strong Pb s I p antibonding character whereas conduction band minimum (CBM) is mostly populated by Pb p state which reflects the unique dual nature i.e ionic and covalent nature of halide perovskite as shown in Fig. 3. It is also demonstrated that electronic

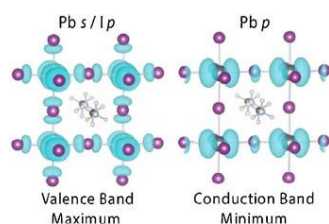


Figure 3: Contribution of s/p orbital from Pb/I near valence band maximum and conduction band minimum is shown.

levels of organic molecule (CH_3NH_3) lies deep within the valence and conduction band indicating the electronic contribution of organic molecule is negligible and the resulting band edges stem from BX_6 octahedra [7]. It is found that the band structure differs slightly when inorganic cation site is replaced by organic cation and the small effect is mainly due to difference in ionic size. Moreover valence band transition changes from $3p \rightarrow 4p \rightarrow 5p$ as the halide ion changes from $\text{Cl} \rightarrow \text{Br} \rightarrow \text{I}$.

Transport properties

Transport studies particularly resistivity and dielectric property in dark and ambient conditions signifies that the crystal structure undergoes two or three phase transitions within a wide temperature regime i.e from 330 K down to 100 K. Moreover since the organic cation has a permanent dipole moment the coupling between the carrier dynamics and the dipole orientational is also studied by dielectric spectroscopy.

The resistivity (ρ) at room temperature is found to be order of $10^9 \Omega \text{ cm}$ which increases by another order of magnitude around 145K. Resistivity at the structural

transition temperatures 236 K and 151 K show a kink as shown by the arrows in the Fig.4. The inset represents the activation energy of charge carriers

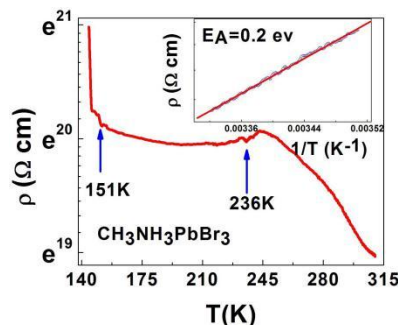


Figure 4: Resistivity at dark condition as a function of temperature. The inset shows the activation energy around room temperature.

around room temperature. In the region $T < 150$ K, resistivity rises sharply with decreasing temperature, while for $151 < T < 240$ K, resistivity shows a weak temperature dependence behavior followed by region $T > 240$ K where it follows an ideal semiconductor behavior. The weak temperature response shows presence of hopping type conduction due to existence of charge trap carriers. Fig. 5 repre-

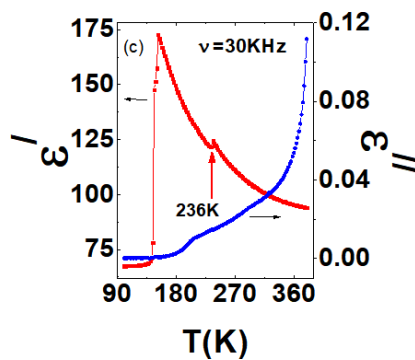


Figure 5: Real and imaginary part of dielectric permittivity as a function of temperature.

sents temperature dependence of real part (ϵ') and imaginary part (ϵ'') of complex permittivity at frequency 30 KHz within temperature range 380–100 K. Two distinct frequency independent peaks, a small peak at 236K and a sharp peak at 151K are observed. At 151 K, the sharp decrease of ϵ' from 172 to 65 reflects first order structural phase transition from tetragonal to orthorhombic which has induced long range orientational order of dipole moments. In addition, for $T > 151$ K ϵ' is seen to decrease continuously with increase in

temperature further following the para-electric behavior.

Recently powder neutron diffraction has given a more detailed insight about

the temperature dependence behavior of organic cation within anionic PbI_3^- network. Quasielastic neutron scattering has also provided deep insight about the rotational dynamics of $(\text{CH}_3\text{NH}_3)^+$ cation [8].

Conclusion

Hybrid Organic-inorganic perovskite has proved to be more versatile and multi-functional. Changing inorganic cation in A site with an organic cation involves van der Waals interaction which is weaker than covalent bonding in the former case. This van der Waals interaction paves new path for atomic reorientation which results in varieties of optical and electrical properties. From band calculation it is found that atomic hybridization mainly occurs between Pb and I s/p orbitals whereas no such participation occurs from organic cation. Moreover hybrid perovskite undergoes series of structural phase transitions as going from high temperature to low temperature. This is further verified by many direct and indirect experimental techniques such as resistivity, dielectric spectroscopy and neutron scattering.

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