

# PEROVSKITES A UNIQUE CLASS OF MATERIALS FOR DEVICES

B. VISWANATHAN

July 11, 2024



# Contents

<b>1</b>	<b>INTRODUCTION</b>	<b>7</b>
1.1	Materials Science An emerging Discipline . . . . .	7
1.2	Properties of Perovskites . . . . .	13
1.3	Applications . . . . .	13
1.4	Perspectives . . . . .	14
1.5	Conclusion . . . . .	16
<b>2</b>	<b>STRUCTURE OF PEROVSKITES</b>	<b>19</b>
2.1	Introduction-The Perovskite Structure . . . . .	19
2.2	Cubic Close Packing (CCP) . . . . .	20
2.3	Voids in crystal: Octahedral (O) and Tetrahedral ( $T_+$ and $T_-$ ) . . . . .	20
2.4	Location of tetrahedral and octahedral sites in an fcc/ccp unit cell . . . . .	21
2.5	$ReO_3$ Structure . . . . .	22
2.6	The Perovskite Structure . . . . .	22
2.7	suggested Reading Resources . . . . .	23
2.8	Distortion in Perovskite Structure . . . . .	23
2.9	Structure of Hybrid Organic-Inorganic Perovskite (HIOP) . . . . .	25
2.10	Suggested Reading Resources . . . . .	26
2.11	$A_2BO_4$ -Layered Perovskite: . . . . .	28
2.12	Double Perovskite, $A_2BB'O_6$ . . . . .	29
2.13	References . . . . .	29
<b>3</b>	<b>APPLICATIONS OF PEROVSKITES</b>	<b>35</b>
3.1	Perovskites in Magnetic Devices . . . . .	35
3.2	Electronic Structure of Perovskites . . . . .	35
3.3	Perovskites in Magnetocaloric Effect Based Magnetic Refrigerators . . . . .	36
3.4	Perovskites in Spintronics . . . . .	37
3.5	Perovskites in Data Storage System . . . . .	38
3.6	References . . . . .	38
<b>4</b>	<b>HYBRID ORGANIC INORGANIC PEROVSKITES - AN INTRODUCTION</b>	<b>41</b>
4.1	Introduction . . . . .	41
4.2	References . . . . .	44
<b>5</b>	<b>PERSPECTIVES ON PEROVSKITES</b>	<b>47</b>
5.1	Perovskite Solar Cells . . . . .	47

<b>6</b>	<b>HYBRID PEROVSKITES - SOLAR CELLS</b>	<b>53</b>
6.1	Hole Transport Layer: . . . . .	55
6.2	Electron Transport Layer: . . . . .	55
6.3	Opto-Electronic Property . . . . .	58
6.4	Factors Influencing the Performance of Perovskite Materials . . . . .	59
6.4.1	Solar Radiation . . . . .	59
6.4.2	Influence of Thickness . . . . .	59
6.4.3	Influence of Defect Density . . . . .	60
6.4.4	Influence of Temperature . . . . .	60
6.4.5	Influence of Moisture Content and Oxygen . . . . .	61
6.4.6	Influence of Other Effects . . . . .	61

# Preface



# Chapter 1

## INTRODUCTION

### 1.1 Materials Science An emerging Discipline

Material Science is the Emerging Discipline in this century, Material Science will dominate the research and application fields due to various reasons, mainly because of their application potential in devices. Materials have been the centre of all human endeavours through all the centuries. In this sense, the ages have also been named after materials such as stone age, bronze age, iron age, and so on and the current time can be called nano-age. The history of materials science is the study of materials of various kinds which are used and employed in the development of society all these days. The development of material science has been the main reason for the culture of the people on this earth. The materials have been the record of the age of the cultures throughout the centuries.

Even though many branches of science have their founding figures, no such single person can be identified as the founding central figure of modern material science. During the second world war, the collaborations of multiple fields of study were needed to produce technological advances which have led to the concept of Material Science and Engineering. After this, the US President Science Advisory Committee (PSAC) came up with the idea of materials as the central factor in the development of space and military technology. Consequent to this, five chosen and major universities in the US were identified as initial centres of research activities in Material Science. This initiative has led to many departments around the world, changing its name to material science. Some new centres have also been formulated in various institutions [1].

Material Science has been revolutionising life on earth, especially in the last few decades. In every sphere of human activity, new materials have changed life style in terms of time and comfort. Metal oxides are a growing set of materials employed in many industrial products, especially in environmental remediation, medical technology, energy conversion, water treatment and personal care products. These applications it is projected, will increase in the coming days. It is stated that three to four new consumer products are introduced every week, employing these solid-state materials.

The known oxide materials assume various structures. Typical oxide systems are assembled in Table 1. Many of these systems are naturally found. Their properties can be effectively utilized in some of the solid-state devices now in use [2].

Among the various solid-state materials, oxides especially the class under the general name “perovskites” have been occupying a central place. Perovskites (mostly mineral of magnesium, silicon and oxygen,  $(\text{MgTiO}_3)$ ) accounts for half of the total mass of the planet earth, and therefore it is the most available material in this world. Earth mantle is supposed to be made up of various kinds of perovskite structure; nobody has yet taken a sample out of it to prove

Table 1.1: Table 1 some of the known Oxide Materials

Name of the structures	Typical examples	Typical uses
Perovskites	$\text{CaTiO}_3$	Solar cells, opto-electronics
Spinel	$\text{Mg}_2\text{AlO}_4, \text{Fe}_3\text{O}_4$	Ferrimagnetism
olivine	$\text{Mg}_2\text{SiO}_4, \text{Fe}_2\text{SiO}_4$	Gemstone
ilmenite	$\text{FeTiO}_3$	Ore for Ti
Fluorite	$\text{CaF}_2$	Fluorescence
Pyrochlore	$(\text{NaCa})_2\text{Nb}_2\text{O}_5\text{F}$	Magnetic property
Garnet	$\text{X}_3\text{Y}_2(\text{SiO})_2$	Magnetic Property
Rutile	$\text{TiO}_2$	semiconductor, Photocatalyst

it. At high pressures, the silicate mineral olivine transforms into ringwoodite spinel structure, and very high pressure transforms it to perovskite structure [3] as shown:  $\text{Mg}_2\text{SiO}_4$  (Olivine)  $\rightarrow$   $\text{SiMg}_2\text{O}_4$  (Spinel)  $\rightarrow$   $\text{MgSiO}_3$  (Perovskite) +  $\text{MgO}$  (Periclase)

Depth (km)	Phase Transformation
Transition Zone	
410	Olivine ( $\alpha\text{-(Mg,Fe)}_2\text{SiO}_4$ ) $\leftrightarrow$ Wadsleyite ( $\beta\text{-(Mg,Fe)}_2\text{SiO}_4$ )
450	Kyanite ( $\text{Al}_2\text{SiO}_5$ ) $\leftrightarrow$ Corundum ( $\text{Al}_2\text{O}_3$ ) + Stishovite ( $\text{SiO}_2$ ) (tetr.)
520	Wadsleyite ( $\beta\text{-(Mg,Fe)}_2\text{SiO}_4$ ) $\leftrightarrow$ Ringwoodite ( $\gamma\text{-(Mg,Fe)}_2\text{SiO}_4$ )
400-600	Pyroxene ( $(\text{Mg,Fe)}_2\text{Si}_2\text{O}_6$ ) $\leftrightarrow$ Majorite ( $\text{Mg}_3(\text{MgSi})\text{Si}_3\text{O}_{12}$ )
Lower Mantle	
670	Ringwoodite ( $\gamma\text{-(Mg,Fe)}_2\text{SiO}_4$ ) $\leftrightarrow$ Perovskite ( $(\text{Mg,Fe})\text{SiO}_3$ ) + Magnesio-wüstite ( $(\text{Fe,Mg})\text{O}$ )
850-900	Pyrope ( $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ) $\leftrightarrow$ Perovskite ( $(\text{Mg,Fe})\text{SiO}_3$ ) + Sodium solution of Corundum ( $\text{Al}_2\text{O}_3$ ) and Ilmenite ( $(\text{Mg,Fe})\text{SiO}_3$ )
1200	Stishovite ( $\text{SiO}_2$ ) $\leftrightarrow$ $\text{SiO}_2$ (CaCl <sub>2</sub> structure)
1700	Metallization of chemical bonds in Wüstite ( $\text{FeO}$ )
2000	$\text{SiO}_2$ (CaCl <sub>2</sub> structure) $\leftrightarrow$ $\text{SiO}_2$ (structure intermediate between PbO and ZrO <sub>2</sub> )
2200-2300	Corundum ( $\text{Al}_2\text{O}_3$ ) $\leftrightarrow$ $\text{Al}_2\text{O}_3$ (Rh <sub>2</sub> O <sub>3</sub> structure)
	D" layer
2800-2900	Complicated phase relations, partial melt
Outer Core	
2900	Liquid Iron

Table 1.2: Depth and Phase Transformations in the Earth's Mantle and Core

Perovskite means calcium titanate ( $\text{CaTiO}_3$ ), a mineral composite first discovered in 1839 composed of calcium, magnesium and oxygen. The family of solid-state materials which poses calcium titanate structure collectively then termed as perovskites. These two terms have been often used interchangeably. The name perovskite gave on behalf of the famous Russian mineralogist, Count Lev Alekseevich Perovski (1792–1856) and the mineral was first found out in the Ural Mountains by Gustav Rose. Victor Goldschmidt in 1926 was the first who identified



the detailed perovskite crystal structure through the work on tolerance factor [4]. Helen Dick Megaw, in 1945 came with a structure derived from X-ray diffraction data for the first time [5]. Table 1.3 represents the evolution of perovskite structure and applications throughout the centuries [6].

Period	Inventor/organization	Description
1839	Gustav Rose (Berlin, Germany)	During an expedition in Russia, he discovered the mineral based on $\text{CaTiO}_3$ in the Ural Mountains. The mineral was named “perovskite” after the Russian mineralogist Lev Aleksevich von Perovski
1892	H.L. Wells, G.F. Campbell, P.T. Walden and A.P. Wheeler/ Sheffield Scientific School (New Haven Conn)	Prepared compounds based on caesium, lead and halides from aqueous solutions.
1947	Philips (Eindhoven, the Netherlands)	Introduced barium titanate for production of condensers
1952	Perovskite introduced into catalysis	Original articles on this regard reported in the several years of 1952[7], 1953[8] and 1965[9].
1955	Western Electric (New York, N.Y.)	Reported the use of ferroelectric crystalline oxides with perovskite structure for fabrication of electromechanical transducers
1957	C.K. Møller/ Chemical Laboratory at the Royal Veterinary and Agricultural College (Copenhagen, Denmark)	Evaluated the microstructure of the compounds produced by H.L. Wells and his collaborators and found that they had a perovskite structure
1957	Siemens (Munich, Germany)	Developed barium titanate-based resistors
1959	Clevite (Cleveland, Ohio)	Introduced perovskite materials in the fabrication of piezoelectric resonators for electromechanical filters.
1962	A.E. Ringwood/ Australian National University (Canberra, Australia)	Proposed that the Earth’s lower mantle is made primarily of $\text{MgSiO}_3$ perovskite.
1964	Compagnie Generale d’Electricité (Paris, France)	Developed perovskite-based solid electrolytes for fuel cells.
1971	Corning Glass Works (Corning) (N.Y.)	Reported the use of perovskite oxides in frits for glass-ceramic articles.
1971	Exxon Research Engineering (Linden, N.J.)	Developed perovskite-based cathode catalysts for electrochemical cells used to convert alcohols into ketones.
1975	Hitachi (Tokyo, Japan)	Manufactured the first gas sensors based on oxide perovskites
1978	D. Weber/University of Stuttgart (Stuttgart, Germany)	Developed the first organic-inorganic halide perovskites
1979	NGK Insulators (Nagoya, Japan)	Introduced a honeycomb structural body based on barium titanate for use as heating element
1981	GTE Laboratories (Waltham, Mass.)	Introduced lasers based on perovskite crystals
1988	Ferranti Plc (Oldham, U.K.)	Developed a superconducting composition with a perovskite Structure
1994	D.B. Mitzi et al. IBM (Yorktown Heights, N.Y.)	Developed luminescent organic inorganic halide perovskites for light-devices

Period	Inventor/organization	description
1996	Boeing North America (Seal Beach Calif.)	Introduced caesium-germanium halide salts with perovskite structure as nonlinear optical crystals for Optoelectronics
1999	Murase Chikao et al., National Institute of Advanced Industrial Science and Technology (Tokyo, Japan)	Created an optical absorption layer for a solar cell using a rare earth oxide having a perovskite crystal structure
2000 and beyond		New processes for fabrication of solar cells based on perovskite materials were developed leading to an increase of activities in this field, the creation of first devices.

A perovskite structure is a substance that has the generic form  $ABX_3$  and the same crystallographic structure as perovskite (the original mineral). In the periodic table shown in Fig. 1.1 the elements that generally occupy the A or B site cationic positions are indicated. It is seen that almost all elements except the ones that exist either in a gaseous or liquid state under normal conditions can occupy either of these two positions in the perovskite structure.

The perovskite lattice arrangement is shown in Fig.1.2. As is usual with structural science and

IA																	0		
H	IIA											B	C	N	O	F	He		
Li	Be											Al	Si	P	S	Cl	Ar		
Na	Mg	IIIA	IVA	VA	VIA	VIIA	← VIII →					IB	IIB	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Tc	I	Xe		
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
Fr	Ra	Ac																	
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			

Figure 1.1: The Periodic Table showing the possible A and B site elements

in crystallography, perovskites can be represented in multiple ways. The simplest way to conceive a perovskite structure is to have a large atomic or molecular cation (positively-charged) of type A in the centre of a cube. The corners of the cube are then occupied by ions of the type B (also positively-charged cations), and the faces of the cube are occupied by the anion X with a negative charge. More on the structure of perovskites will be dealt with in the subsequent chapters.

Various oxide compounds are known to belong to a few perovskite-based homologous series, such as  $A_{n+1}B_nO_{3n+1}$  Ruddlesden-Popper,  $A_nB_nO_{3n+1}$  Dion-Jacobson,  $Bi_2A_{n-1}B_nO_{3n+3}$  Aurivillius series and some others. The perovskite structures exist in different forms such as:

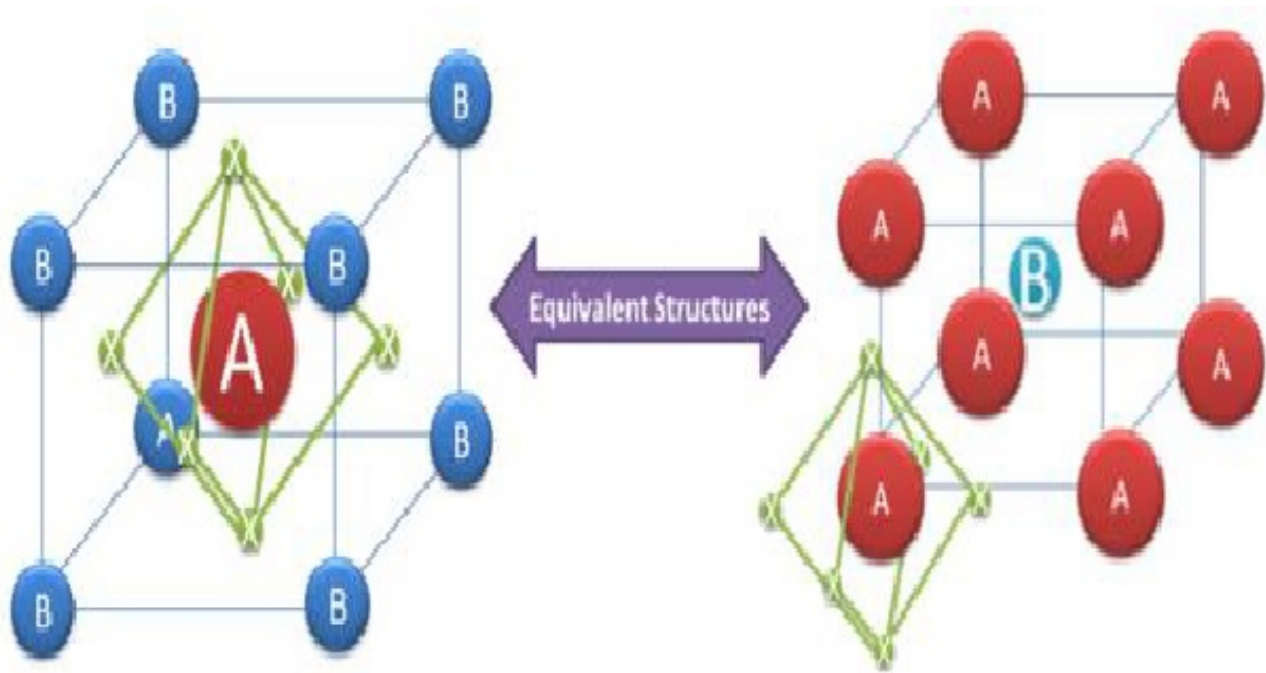


Figure 1.2: Two equivalent structures of perovskite structures with left-hand side is drawn with B site ion at  $\langle 0,0,0 \rangle$  and the right-hand diagram with A site ions at  $\langle 0,0,0 \rangle$  position [10].

$ABO_3$  perovskite (ex:  $BaTiO_3$ ,  $CaTiO_3$ ),  $A_2BO_5$  Layered perovskite (ex:  $Sr_2RuO_4$ ,  $K_2NiF_4$ ),  $A_2BB'O_6$  Double perovskite (ex:  $Ba_2TiRuO_6$ ) and  $A_2A'B_2B'O_9$  Triple perovskite (ex:  $La_2SrCo_2FeO_9$ ). Several perovskite-type oxides have been extensively studied due to their new properties including superconductivity, insulator-metal transition, ionic conduction characteristics, dielectric properties, optoelectronic property and ferroelectricity. Perovskite is one of the most frequent studied structures in solid-state chemistry, and it accommodates as stated above, most of the metal ions in the periodic table with a significant number of different anions. During the last few years, many investigations were focused on the study of perovskite solids, typically  $ABO_3$ . These solids are currently gaining considerable importance in the field of electrical ceramics, refractories, geophysics, material science, astrophysics, particle accelerators, fission-fusion reactors, heterogeneous catalysis, environment and others. Perovskite structured oxides can accept considerable substitutions in one or both cationic sites (i.e. A and B sites) while retaining their original crystal structures. Such a feature provides the chemical tailoring of the materials via partial replacement of the cationic site(s) with foreign metal ions, hence modifying their structural, microstructural, electrical and magnetic properties. Perovskite-type oxides and perovskite-like oxides have found many applications in physics and chemistry. The physicochemical and device application properties of perovskites are dependent on the crystal structure, lattice defect, exposed lattice plane, surface morphology, particle size, and specific surface area as well as the porous texture. The cubic perovskite is called the ideal one. This class of materials has excellent potential for a variety of device applications due to their simple crystal structures and unique ferroelectric and dielectric properties. Perovskite systems can crystallise in a variety of compositions. There can be a variety of combinations of cations like  $A^+B^{5+}$ ,  $A^{2+}B^{4+}$ ,  $A^{3+}B^{3+}$  and a host of defect compositions in  $ABX_3$  systems. The following flow diagram (Fig.1.3.) with examples demonstrates this concept [11-12].

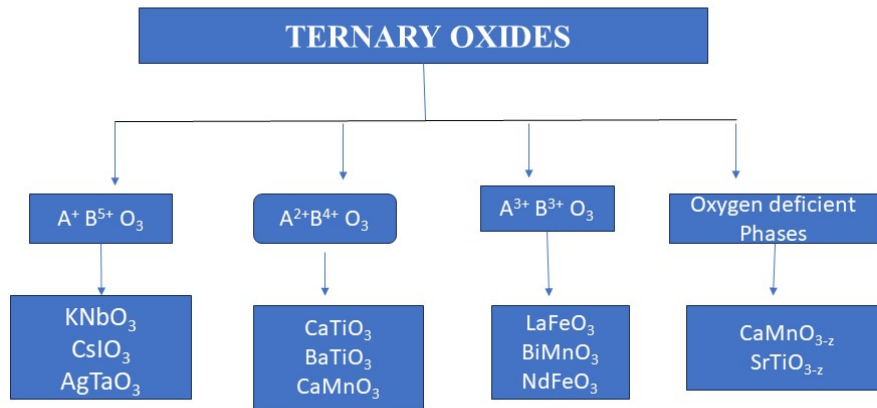


Figure 1.3: Flow diagram of the generation of variety of compositions in  $ABX_3$  systems [11]

## 1.2 Properties of Perovskites

Perovskites is a derivative of the close packed structure in which the oxide ions are arranged in a cubic close packed arrangement except one oxide ion is missing in every second layer leaving a large volume empty in the centre. The  $Ti^{4+}$  ion occupies at the octahedral interstices, and the large cation  $Ca^{2+}$  fills the vacant cavity created in the centre by the missing of oxide ion with a coordination number 12. The ability of perovskite to accommodate large cations of rare earth element makes it as a unique among the close-packed oxides. If the 12-coordinated cation is smaller compared to the oxide ion, the tilting of octahedra distorts the perovskite structure. It usually takes place at a lower temperature and giving rise to many phase transformations. The modified structure produced after tilting could be tetragonal, orthorhobic or monoclinic or sometimes without any centre of symmetry. Non-centric perovskites display piezoelectricity or ferroelectricity, and synthetic perovskites used as electronic sensors. The structure of newly discovered high-temperature superconductors show resemblance to perovskite structure. In these superconducting materials Cu substitutes Ti in the layers and shows superconductivity at slightly elevated temperatures.

## 1.3 Applications

Perovskite materials find application in many devices' manufacture. Inorganic perovskite oxides are fascinating materials due to its very stable structure, the possibility of generating a large number of compounds, variety of surface and bulk properties and find many applications. These solids are currently gaining considerable importance in the field of electronics, geophysics, astrophysics, nuclear, optics, optoelectronics, environment, solar cells and catalysis. Perovskite-phase metal oxides exhibit a variety of interesting physical properties which include ferroelectric, dielectric, pyroelectric, piezoelectric, superconductivity, multiferroic, proton conducting, Colossal Magnetoresistance (CMR), Giant Magnetoresistance (GMR), mixed conduction, catalytic behaviour and solar energy conversion. Depending on these distinct properties perovskite

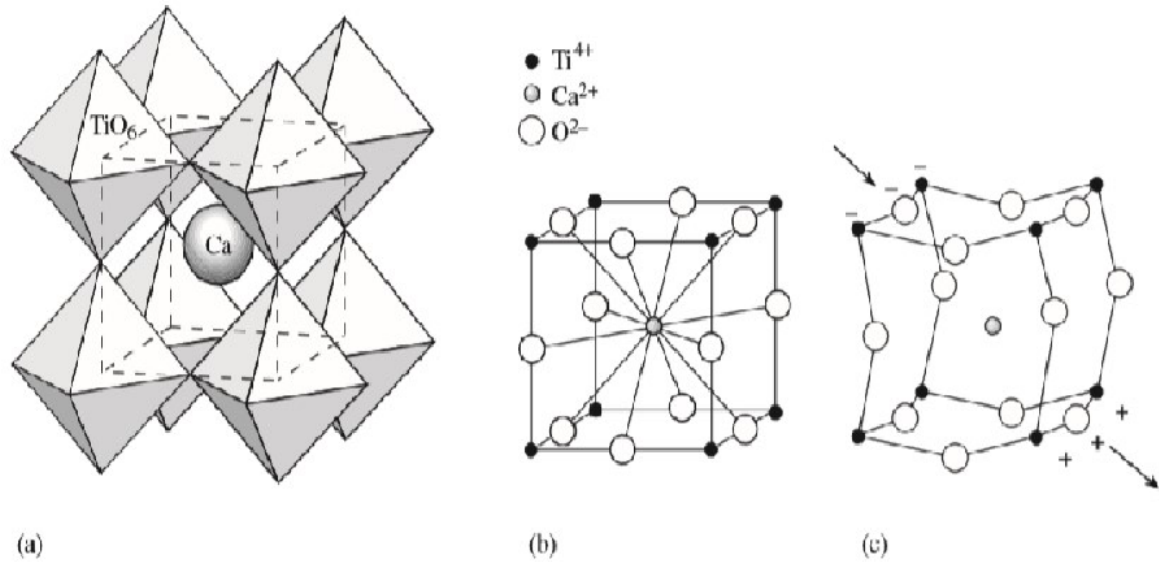


Figure 1.4: (a) Polyhedral representation of the structure of perovskite, showing the large 12-fold coordinated  $\text{Ca}^{2+}$  in the centre of the cubic unit cell and the smaller 8-fold coordinated  $\text{Ti}^{4+}$  in the corners. (b) Representation of perovskite structure with small spheres. (c) The perovskite structure distorts when stress is applied, creating an electric field (piezoelectricity). Reproduced from [3]

systems find use in various device applications such as (1) Thin film capacitors (2) Non-volatile memories; (3) Photoelectrochemical cells; (4) Recording applications (5) Read heads in hard disks, (6) Spintronics devices (7) Laser applications, (8) For windows to protect from high-temperature infrared radiations, (9) High temperature heating applications (Thermal barrier coatings) (10) Frequency filters for wireless communications (11) Non-volatile memories (12) Sensors, actuators and transducers, (13) Drug delivery, (14) Catalysts in modern chemical industry (15) Ultra-sonic imaging, ultra-sonics and underwater devices, (16) microwave devices and so on. Perovskites exhibit many new and unique properties, and some of the properties exhibited by typical perovskites are assembled in Table .4

## 1.4 Perspectives

Perovskites are unique today among all the known solid-state materials with a variety of applications contrasting in a property like highly resistive (Positive temperature coefficient materials) to highly conducting materials (superconductor). As stated above nearly all the elements can be included in the perovskite structure, and since this structure tolerates partial substitution at both the cationic sites and several anions can be placed in the perovskite composition, the number of materials that can be obtained in perovskite composition appears to be in numerous. Many of these perovskite materials are revolutionising the application potential and are becoming competitive to the existing materials like silicon for solar cell application.

The flexibility of the  $\text{ABO}_3$  perovskite crystal structure and the possibility to include a wide range of cations with different oxidation states as well as cation or anion vacancies are responsible for the variety of perovskite-based compounds with a wide range of physical properties. Due to the number of applications and utility in the different fields, there is a need to study the perovskite structured materials with improved properties, and this can be realized through

Comounds	Properties	Applications	Notes
BaTiO <sub>3</sub>	Ferroelectricity piezoelectricity high dielectric constant	Multilayer Ceramic capacitors (MLCCs) PTCR resistors embedded capacitance	most widely used dielectric ceramic T <sub>c</sub> = 125 <sup>0</sup> C
(Ba, Sr) TiO <sub>3</sub>	Non-linear dielectric Properties	Tunable microwave devices	Used in th paraelectric state
(Pb, Zr) TiO <sub>3</sub>	Ferroelectricity, piezoelectricity	piezoelectric transducers and actuators erroelectric memorie (FERAMs)	PZT most successful successful Piezoelectric Material
Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub>	Ferroelectric with high Curie Temperature (T <sub>c</sub> )	High-temperature actuators, FeRAMs	Aurivillius compound T <sub>c</sub> = 675 <sup>0</sup> C.
(K <sub>0.5</sub> Na <sub>0.5</sub> NbO <sub>3</sub>	ferroelectricity, piezoelectricity	lead free Piezoceramics	perormance not yet comparable to PZT but progress
(Pb,La)(Ti,Zr)O <sub>3</sub>	Transparent ferroelectric	optoelectroic devices	first transparent ferroelectric ceramic
BiFeO <sub>3</sub>	Magnetoelectric coupling, high Curie temperature	Magnetic field detectors, memories	Most investigated multiferroic compound T <sub>c</sub> = 850 <sup>0</sup> C
PbMg <sub>1/3</sub> Nb <sub>2/3</sub> O <sub>3</sub>	Relaxor ferroelectric	Capacitors, actuators	High permittivity significantelectrorestictiv ccoefficients, frequency dependent properties
SrRuO <sub>3</sub>	Ferromagnetism	Electrode material for epitaxial ferroelectric thin films	
()La, A) MnO <sub>3</sub>	Ferromagnetism, giant magnetoresistance, spin polarised electrons	Magnetic field sensors, spin electronic devices	
SrTiO <sub>3</sub>	Incipient ferroelectricity thermoelectric power Metallic electronic conduction when n doped mixed conduction when p doped, photocatalyst	alternative gate dielectric material barrier layer capacitors, a substrte for epitaxial Growth photo-assisted water splitting	multifunctional materials
LaGaO <sub>3</sub> BaIn <sub>2</sub> O <sub>5</sub>	Oxide-ion conductio	he electrolyte in solid oxide fuel cells (SOFCs)	BaIn <sub>2</sub> O <sub>5</sub> is an oxygen-deficient perovskite with Brownmillerite structure
BaCeO <sub>3</sub> , BaZrO <sub>3</sub>	Proton conduction	The electrolyte in protonic solid oxide fue cells(PSOFCs)	High protic conduction at 500 -700 <sup>0</sup> C
(La, Sr) BO <sub>3</sub>	Mixed conduction catalyst	The cathode material in SOFCs, oxygen separation membranes Membrane reactors Controlled oxidation of hydrocarbons	used in SOFC cathodes
LaAlO <sub>3</sub> , YAlO <sub>3</sub>	Host materials for rare earth luminescent ions	Lasers Substrates for epitaxial film deposition	

new synthesis strategy and using different valence cations or anions and dopants.

The possibility of including organic cations like methylammonium and a host of other organic cations impart to the resulting system a variety of properties. The ionic radius of such organic cations has a high bearing on the properties of resultant perovskites. This concept of structures based on the ionic radius and their radius ratio has to be modified concerning the crystallisation of hybrid organic-inorganic perovskites, and these aspects require careful consideration.

## 1.5 Conclusion

The crystallization in perovskite structure is considered in terms of tolerance factor defined, in terms of cation and anion radii, and the universal applicability of this concept for adopting perovskite structure needs a careful examination. There are a variety of questions that one can have on perovskite materials like why the anion oxide perovskites are so crucial in the application field or why other compositions also crystallise in perovskite structure? The complete understanding of these aspects will be essential for exploiting them in the application field.



# Bibliography

- [1] Cahn, R. W. (Ed.). *Chapter 1 - Introduction. In: The Coming of Materials Science (Vol. 5, pp. 3–17)*. Pergamon, 2001.
- [2] Yuanbing Mao, Hongjun Zhou, Stanislaus S. Wong. Synthesis, Properties, and Applications of Perovskite-Phase Metal Oxide *Nanostructures, Material Matters*, 2010, **5**(2), 50.
- [3] Hans-Rudolf Wenk, Andrey Bulakh. Chapter 25 - Oxides and hydroxides. Review of ionic crystals. In: *Minerals: Their Constitution and Origin*, Cambridge University Press, 2004.
- [4] Goldschmidt, V. M. (1926). Die Gesetze der Krystallochemie. *Naturwissenschaften*, 14(21), 477–485.
- [5] Megaw, H. Crystal Structure of Barium Titanate. (1945). *Nature*, **155**(3938), 484–485.
- [6] Gagliardi, M. Perovskite Solar Cells: Materials, Fabrication, and Global Markets, BCC Research, <https://bit.ly/2YeJ8s5>
- [7] Parravano, G. (1952). Ferroelectric Transitions and Heterogeneous Catalysis. *The Journal of Chemical Physics*, **20**(2), 342–343.
- [8] Parravano, G. (1953). Catalytic Activity of Lanthanum and Strontium Manganite. *Journal of the American Chemical Society*, **75**(6), 1497–1498.
- [9] Dickens, P. G., & Whittingham, M. S. (1965). Recombination of oxygen atoms on oxide surfaces. Part 2. Catalytic activities of the alkali metal tungsten bronzes. *Transactions of the Faraday Society*, **61**, 1226–1231.
- [10] Perovskites and Perovskite Solar Cells: An Introduction, <https://bit.ly/2a4utpF>
- [11] Jadhav, K. M. Investigations of electrical and magnetic properties of some perovskite structured materials, PhD Thesis, Dr. Babasaheb Ambedkar Marathwada University, 2017. <https://bit.ly/2X81AJ0>
- [12] Rama Murthy P. S. Study of structural, transport and magnetic properties of some perovskite based oxides, PhD Thesis, Goa University, 2010.



# Chapter 2

## STRUCTURE OF PEROVSKITES

### 2.1 Introduction-The Perovskite Structure

The perovskite has general formula  $ABX_3$ . The 'ideal' perovskite structure, illustrated in Fig. 1a is cubic with atoms at the corners, edge centre and body centre. This structure is adopted by complex halides and by many complex oxides. The latter are very numerous because the sum of the charges on A and B (+6) may be made of 1+5, 2+4, or 3+3. The structure includes mixed oxide type materials such as  $SrTiO_3$ ,  $CaTiO_3$ ,  $SrZrO_3$ ,  $SrHfO_3$ ,  $SrSnO_3$ , and  $BaSnO_3$ . A unit cell of  $SrTiO_3$  is shown in Fig. 1b, this unit cell is known as the A-type because, if we take the general formula  $ABX_3$  for the perovskites, then the A atom is at the centre in this cell. The central Sr(A) atom is coordinated to 8 Ti (B) atoms at the corners and 12 oxygens (X) at the centre of the cell edges. The structure can be usefully described in other ways. First, it can be described as a ccp/fcc (cubic close packing/face-centred cube) array of A and X atoms with the B atoms occupying the octahedral hole. Second, perovskite has the same octahedral framework as  $ReO_3$  based on  $BX_6$  octahedra with an A atom added in at the centre of the cell.

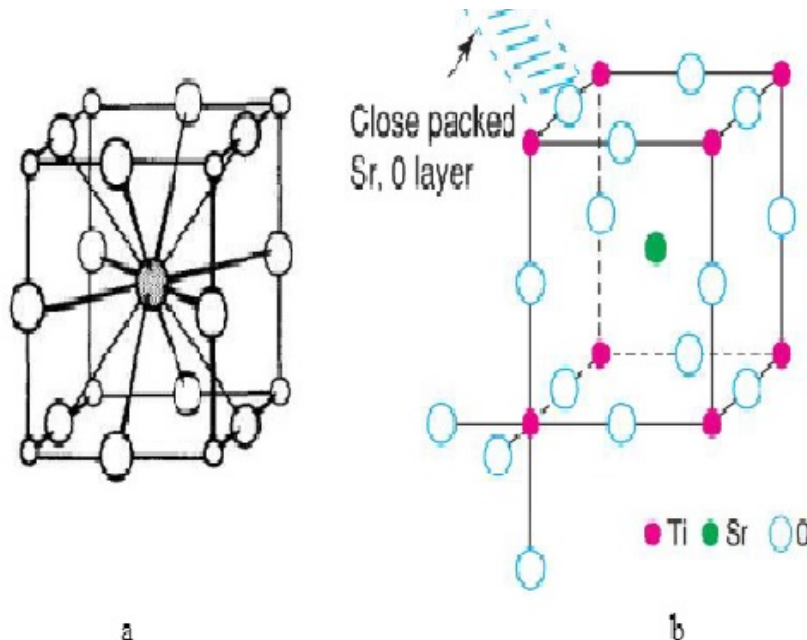


Figure 2.1: (a) Unit cell of cubic perovskite structure [1]; (b) unit cell of  $SrTiO_3$  [2].

To understand the perovskite structure in detail, we need to understand a few basics such as ccp (cubic close packing), voids concept and structure of  $ReO_3$ . This will help us view perovskite structure from a different point of view for better visualisation.

## 2.2 Cubic Close Packing (CCP)

During crystal growth, the atoms arrange in different ways to give crystal. For our understanding, let us arrange atoms layer by layer. Atoms in the first layer (layer A) can be arranged/packed in two different ways; a) a square array of spheres; b) a close-packed layer of spheres as shown in Fig. 2a and b. The close packing can be visualised as a squeezed square layer. To build up a close-packed structure in three-dimensions, we must now add a second layer (layer B). The spheres of the second layer sit in half of the hollows of the first layer; these have been marked with dots and crosses. The layer B in Fig. 3 sits over the hollows marked with a cross (although it makes no difference which type we chose).

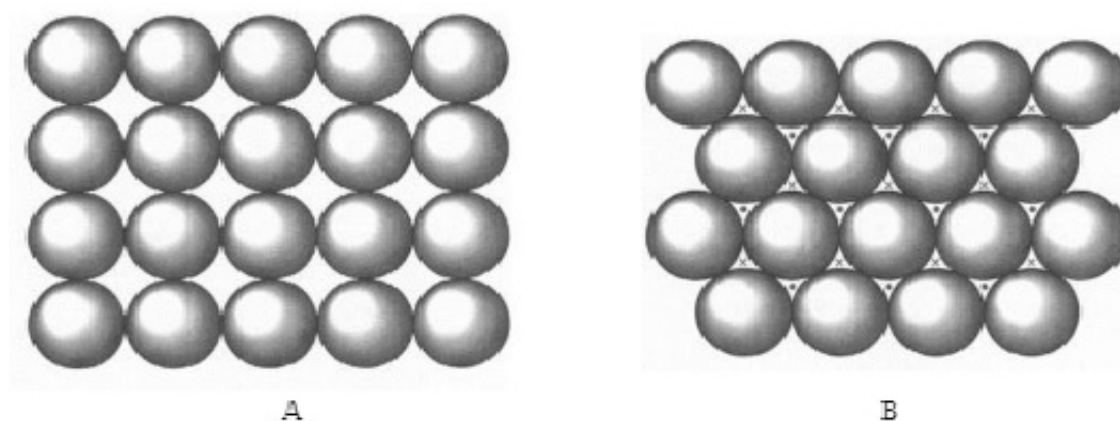


Figure 2.2: A square array of spheres; (b) a close-packed layer of spheres.[3]

When we add a third layer, it could be positioned over those hollows marked with a dot. This third layer, which we could label C, would not be directly over either A or B layer and the, stacking sequence when repeated would be ABC ABC AB...and so on. This is known as cubic close-packing (ccp) (Fig. 4) (The name cubic arise from the resulting symmetry of the structure). In a 3D close packed structure, each sphere is in contact with with 12 others, and this is the maximum coordination number possible for contacting and equal-sized spheres. Close-packing represents the most efficient use of space when packing identical spheres—the spheres occupy 74% of the volume: the packing efficiency is said to be 74%. Each sphere in the structure is surrounded by twelve equidistant neighbours—six in the same layer, three in the layer above and three in the layer below: the coordination number of an atom in a close-packed structure is thus 12 as shown in Fig. 5 (a).

The unit cell of a ccp arrangement is the familiar face centred cubic (fcc) unit cell, Fig. 5 (b), with spheres at corner and face centre positions.

## 2.3 Voids in crystal: Octahedral (O) and Tetrahedral ( $T_+$ and $T_-$ )

An important feature of close-packed (cp) structures is the shape and number of the small amounts of space trapped in between the spheres. Two different types of spaces are contained within a close-packed structure: a) octahedral void and b) tetrahedral void. Firstly, the octahedral void is the space present between six spheres of two cp layers A and B: three spheres in

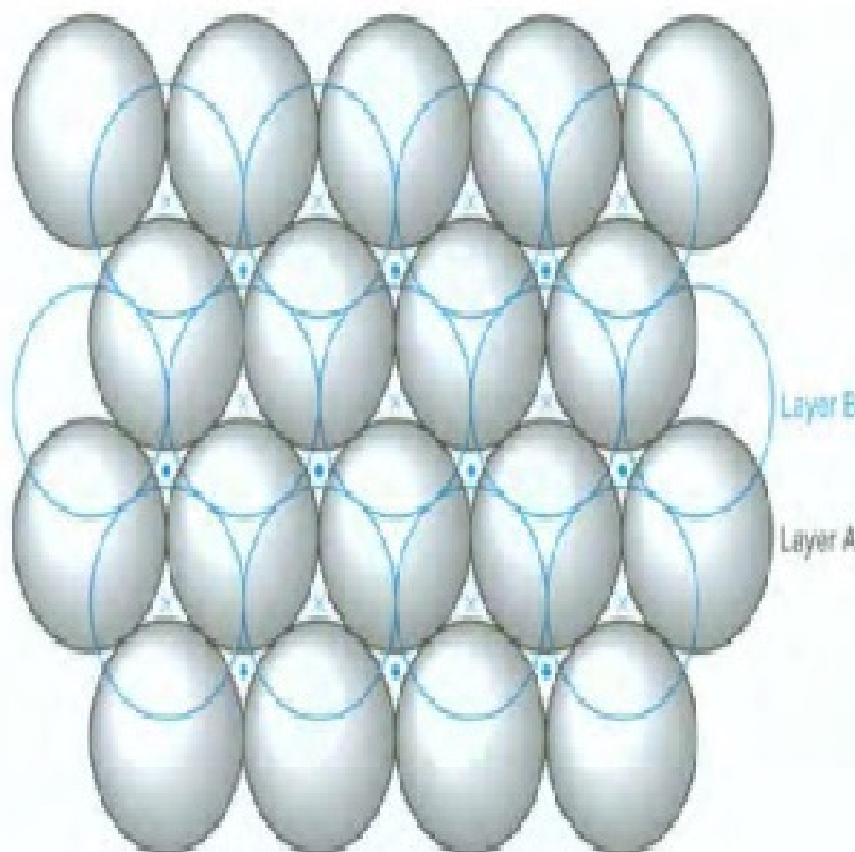


Figure 2.3: Two layers of close-packed spheres.[3]

layer A and three in layer B, as shown in Fig. 6a and b. The centres of these spheres lay at the corners of an octahedron, hence the name. If  $n$  spheres are in the array, then there are also  $n$  octahedral holes. Whereas, the tetrahedral void is the space present between four spheres of two cp layers A and B, wherein three spheres that form the base of the tetrahedron belong to one cp layer with the apex of the tetrahedron either in the layer above or below. This gives two orientations of tetrahedral sites,  $T_+$  and  $T_-$ , in which the apex is up and down, respectively as shown in Fig. 6a and c, with centres of the spheres at the corners of a tetrahedron hence the name. If  $n$  spheres are in the array, then there are  $2n$  tetrahedral holes. No. of octahedral voids with  $n$  atoms =  $n$  atoms No. of tetrahedral voids with  $n$  atoms =  $2n$  atoms. Since there are 4 atoms in a ccp/fcc unit cell, hence there are 4 octahedral voids and 8 tetrahedral voids in a ccp/fcc unit cell..

## 2.4 Location of tetrahedral and octahedral sites in an fcc/ccp unit cell

It is important to visualise and understand the locations of these voids ( $T_+$ ,  $T_-$ , and O) in a unit cell since in crystals these voids are generally occupied by small ions/cations. As shown in Fig. 7, an fcc (face-centered cubic) or ccp (cubic close-packed) unit cell has anions, X, at the corners and face centers (A, B, C, and D). The octahedral sites are easiest to locate; they are at edge-center (positions 1, 2, 3) and body-center (position 4). If the unit cell has length  $a$ , the M-X distance for octahedral sites is  $\frac{a}{2}$ . To see the  $T_+$  and  $T_-$  sites clearly, it is convenient

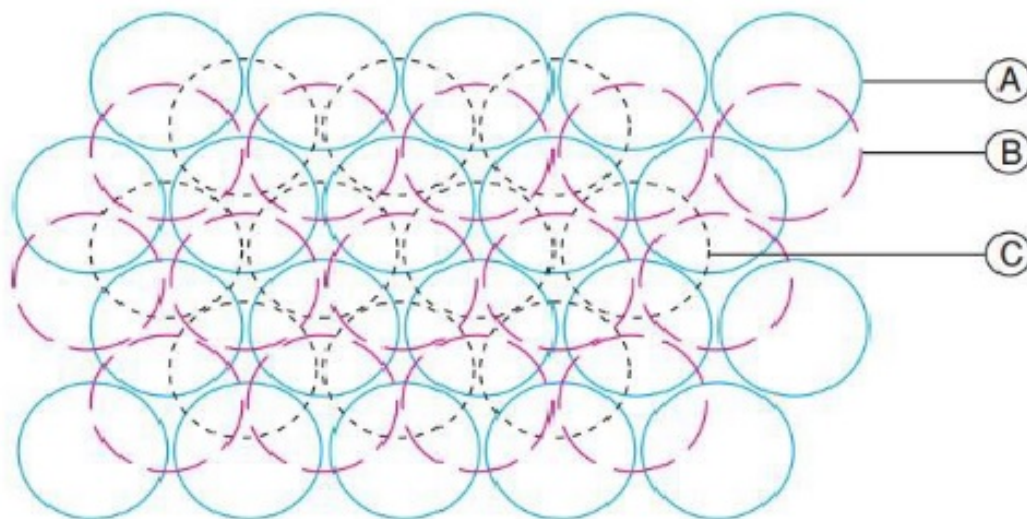


Figure 2.4: Cubic close-packing (ccp) with ABC layer sequence.[2]

to divide the unit cell into eight mini-cubes by bisecting each cell edge (dashed lines). These mini-cubes contain anions at only four of the eight corners; in the middle of each mini-cube is a tetrahedral site, either  $T_+$  or  $T_-$ .

## 2.5 $\text{ReO}_3$ Structure

It is a primitive cube structure consisting of  $\text{ReO}_6$  octahedra linked together through each corner to give a highly symmetrical three-dimensional network. Part of the structure with single octahedral coordination is given in Fig. 8a, and the linking of the octahedra in 8b.

## 2.6 The Perovskite Structure

: Through  $\text{ReO}_3$  structure and CCP/FCC and voids Perovskite has primitive cubic unit cell and octahedral framework as  $\text{ReO}_3$  based on  $\text{BX}_6$  octahedra. With an A atom added in at the centre of the unit cell of  $\text{ReO}_3$  we will get perovskite structure. For example-  $\text{SrTiO}_3$  as shown in Fig. 9a, with Sr atoms occupying the body center  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , Ti atoms occupying cube corners  $(0,0,0)$  and oxygen atoms occupying edge centers  $(\frac{1}{2}, 0, 0; 0, \frac{1}{2}, 0; 0, 0, \frac{1}{2})$ . The 3D and 2D-view of  $\text{SrTiO}_3$  structure are shown in Fig. 9a and b. O has two  $T_+$  as its nearest cationic neighbors, whereas Sr is coordinated with 8 Ti atoms and 12 oxygen atoms.  $\text{SrTiO}_3$  can also be represented as a ccp/fcc array Sr and O, with Sr occupying cube corners and O at face centers and with the Ti atoms occupying the body center octahedral void of fcc lattice as shown in Fig. 10a and b. The two descriptions in Fig. 9a and 10a are interchangeable and are simply related by translation of the origin half way along the cube body diagonal.

Perovskite is also regarded as a framework structure with corner-sharing  $\text{TiO}_6$  octahedra and with Sr in 12-coordinate interstices. The octahedral coordination of one Ti is shown in Fig. 11; each O of this octahedron is shared with one other octahedron, such that the Ti-O-Ti arrangement is linear. Thus, octahedra link at their corners to form sheets, and neighbouring sheets link similarly to form a 3D framework.

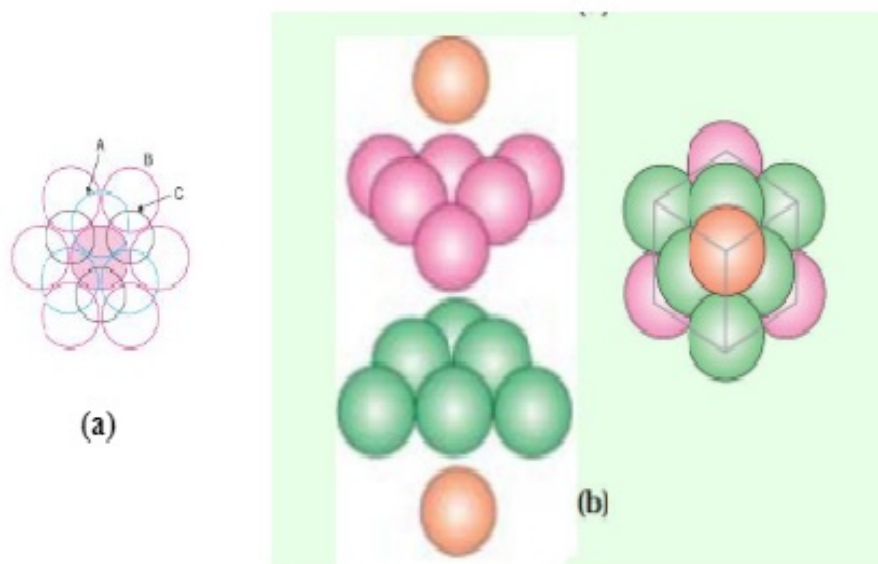


Figure 2.5: (a) Coordination number 12 of the shaded sphere in ccp; [2] (b) face centred cubic (fcc) formed from ccp. [4]

## 2.7 suggested Reading Resources

1. Wells, A.F., (2012). Structural inorganic chemistry. Oxford university press.
2. West, A.R., (2014). Solid state chemistry and its applications. John Wiley and Sons.
3. Smart, L.E. and Moore, E.A., (2016). Solid state chemistry: an introduction. CRC Press.
4. Chemistry class 12th PART 1 ncert, 2017.

## 2.8 Distortion in Perovskite Structure

The 'ideal' perovskite structure, illustrated in Fig. 9, is cubic, with A surrounded by 12 O and B by 6 O. Comparatively few compounds have this ideal cubic structure, many (including the mineral perovskite,  $\text{CaTiO}_3$ ; itself) having slightly distorted variants with lower symmetry. Some examples are listed in Table 1. These departures from the most symmetrical structure are of great interest because of the dielectric and magnetic properties of these compounds. For example, many are ferroelectric, notably  $\text{BaTiO}_3$ , some are anti-ferroelectric, for example,  $\text{PbZrO}_3$  and  $\text{NaNbO}_3$ , and ferromagnetic ( $\text{LaCo}_{0.7}\text{Mn}_{0.3}\text{O}_3$ ) and anti-ferromagnetic ( $\text{GdFeO}_3$ ,  $\text{LaFeO}_3$ , etc.) compounds are known.

In order to understand the distortions from the ideal cubic structure these oxides  $\text{ABO}_3$  were first regarded as purely ionic crystals. From the geometry of the structure it follows that for the 'ideal' structure there is the following relation between the radii of the A, B, and  $\text{O}^{2-}$  ions as shown in equation (1): wherein  $r_A$ ,  $r_B$  and  $r_X$  are ionic radius of A-site cation, B-site cation and X is anion ( $\text{O}^{2-}$ , halogens etc).

$$r_A + r_X = \sqrt{2}(r_B + r_X) \dots\dots\dots 1)$$

Actually the cubic perovskite structure or slightly deformed variants of it are found for ions which do not obey this relation exactly, and this was expressed by introducing a 'tolerance factor', the ratio of ionic sizes that perovskite architectures can tolerate is indicated by the Goldschmidt tolerance factor (t) as shown in equation (2) and (3):

$$r_A + r_X = t\sqrt{2}(r_B + r_X) \quad (2) \quad (2.1)$$

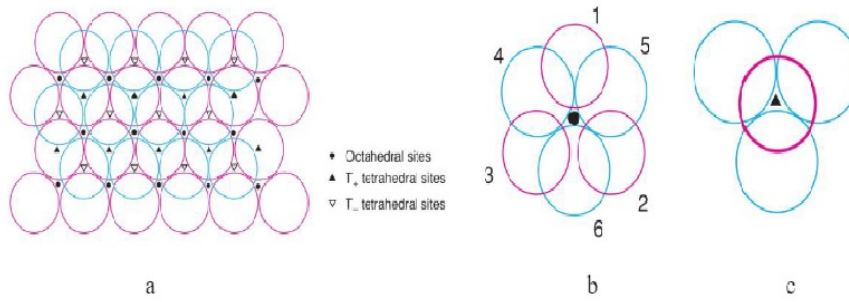


Figure 2.6: (a) Two cp layers showing octahedral and tetrahedral spaces; (b) octahedral void formed with 6 spheres; (c) tetrahedral void formed with 4 spheres.[2]

$$\text{Tolerance factor } t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (3) \quad (2.2)$$

In practice, there is some flexibility over bond lengths and usually, a cubic perovskite forms with  $t$  in the range 0.9 is less than or equal to  $t$  is less than or equal to 1.0. For  $t$  greater than 1, the B site is larger than required. If  $t$  is only slightly greater than 1.0, the structure distorts but is still basically a perovskite as in  $\text{BaTiO}_3$ ,  $t$  less than 1.06 as shown in Fig. 12a. The shifts of Ti and Ba are conventionally shown relative to the  $\text{O}_6$  octahedra around the original Ti position. In  $\text{BaTiO}_3$  Ti shifts by 0.12 Å and Ba in the same direction by 0.06 Å. The Ti environment in the crystal is shown in Fig. 12b, wherein Ti is displaced from the centre of its octahedron giving one short Ti-O distance of 1.86 Å, when compared to the mean value of 1.97 Å in rutile. this distortion has negligible effect on the twelve Ba-O distances. These distortions are the cause of ferroelectric behavior of  $\text{BaTiO}_3$ .

For smaller tolerance factors,  $0.85 < t < 0.90$ , several different kinds of structural distortions occur, as in  $\text{GdFeO}_3$ , the A cation is too small for its site. These distortions generally involve tilting and rotation of the  $\text{BO}_6$  octahedra as shown in Fig. 13. Consequently some, or all, of the B-O-B linkages are no longer linear but are zig-zag, which has the effect of reducing the size of the A cation site. The fact that the structures of compounds  $\text{ABO}_3$  are dependent not only on size factors but also on the nature of B has been demonstrated in many comparative studies. For example, while  $\text{AFeO}_3$  (A = lanthanide) all have perovskite-type structures this is true for  $\text{AMn}^{3+}\text{O}_3$  only if A is La or Ce. The compounds in which A = Ho-Lu adopt a new hexagonal structure with 5- and 7-coordination of A site.



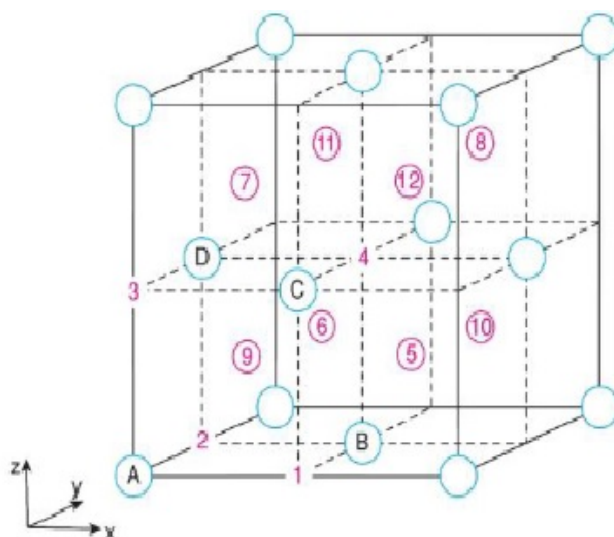


Figure 7. Available void/sites, 1–12, in an fcc/ccp array.[2]

Figure 2.7: caption required

Table 2.1: Compounds with the perovskite type of structure [1]

Ideal cubic structure	SrTiO <sub>3</sub> , SrZrO <sub>3</sub> , SrHfO <sub>3</sub> , SrSnO <sub>3</sub> , SrFeO <sub>3</sub> , BaZrO <sub>3</sub> , BaHfO <sub>3</sub> , BaSnO <sub>3</sub> , BaCeO <sub>3</sub> , EuTiO <sub>3</sub> , LaMnO <sub>3</sub>
At least one form with distorted small cell ( $a = 4 \text{ \AA}$ ): Cubic (C) Tetragonal (T) Orthorhombic (O) Rhombohedral (R)	BaTiO <sub>3</sub> (C, T, O, R) KNbO <sub>3</sub> (C, T, O, R) KTaO <sub>3</sub> (C, ?) RbTaO <sub>3</sub> (C, T) PbTiO <sub>3</sub> (C, T)
Distorted multiple cells	CaTiO <sub>3</sub> , NaNbO <sub>3</sub> , PbZrO <sub>3</sub> , PbHfO <sub>3</sub> , LaCrO <sub>3</sub> , low-PbTiO <sub>3</sub> , low-NaNbO <sub>3</sub> , high-NaNbO <sub>3</sub>

## 2.9 Structure of Hybrid Organic-Inorganic Perovskite (HIOP)

Hybrid organic–inorganic perovskites (HOIPs) are a subclass of ABX<sub>3</sub> materials in which the A-site and/or X-site ions are replaced by organic amine cations and/or organic linkers, respectively. The organic components in the structure of these HOIPs introduce additional functionalities and structural flexibility that cannot be achieved in purely inorganic perovskites. Most importantly, their diverse structural and chemical variability offers substantial opportunities for tuning and modulating their physical properties by facile chemical modification. Hybrid perovskites were structurally characterized in 1978, with the report of the cubic phases of MAPbX<sub>3</sub> (MA = methylammonium and X = Cl, Br or I) as shown in Fig. 14.

By extending the X-site from a single halide to bridging molecular linkers, such as azide (N<sup>3-</sup>), cyanide (CN<sup>-</sup>) and borohydride (BH<sub>4</sub>)<sup>-4</sup>, other families of HOIPs have been formed. The introduction of additional organic components in to the X-site gives another variety of HOIP derivative, namely metal–organic framework perovskites as shown in Fig.15. Metal formate and metal dicyanamide perovskites are well-known examples, in which the A-sites are amine cations and X-sites are (HCOO)<sup>-</sup> or N(CN)<sup>2-</sup> respectively. The abundant variations of

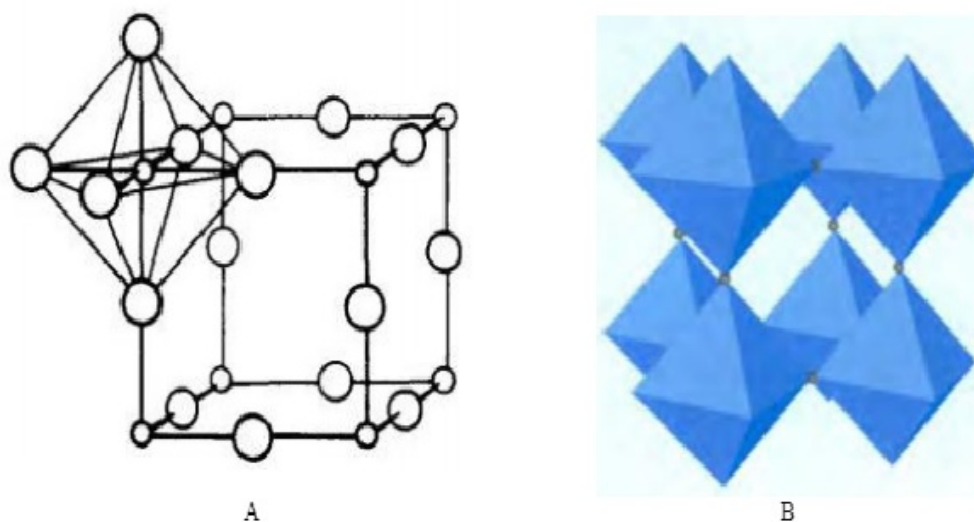


Figure 2.8: (a) a ReO<sub>3</sub> structure; [2] (b) ReO<sub>3</sub> structure showing the linking of [ReO<sub>6</sub>] octahedra. [3]

organic components and metal salts offer enormous chemical possibilities for creating HOIPs, and, hence, this class of materials now spans a considerable part of the periodic table. For the 3D perovskites, the size of the organic A cation is limited by the size of the 3D hole into which it must fit. For a perfectly packed perovskite structure the geometrically imposed condition for the A, M, and X ions to be in close contact is given by equation 2 and 3 (tolerance factor) ‘t’ must satisfy  $t < 1$ . Empirically it is found that  $0.8 < t < 0.9$  for most cubic perovskites, although there is a slightly expanded range for distorted structures. Using  $t$  equal to 1 and essentially the largest values for  $r_B$  and  $r_X$  (e.g.  $r_{Pb} = 1.19$ ,  $r_I = 2.20$  Å), the limit on  $r_A$  is found to be approximately 2.6 Å. Consequently, only small organic cations (i.e. those consisting of three or less C-C or C-N bonds) are expected to fit into the structure. The possible A site, B site and X site combinations are presented in Fig. 16 in HOIPs, a significant number of tolerance factors are found to lie in the range approximately 0.8 to 1.0 as shown in Table 2. These results are similar to those for conventional perovskites and demonstrate the extended validity of the Goldschmidt tolerance factors. In addition, it is evident that the packing density has a pivotal role in the formation of HOIPs. Moreover, this simple semi-empirical approach for assessing size compatibility can guide the rational design and synthesis of new HOIPs using compositions with desired functionalities.

AZE, azetidinium; BTBA, benzyltributylammonium; BTEA, benzyltriethylammonium; DABCO, 1,4-diazabicyclo[2.2.2]octane; DMA, dimethylammonium; EA, ethylammonium; FA, formamidinium; GUA, guanidinium; HAZ, hydrazinium; HIM, imidazolium; HOIPs, hybridorganic-inorganic perovskites; MA, methylammonium; PIP, piperazinediium; PPN, bis(triphenylphosphoranylidene)ammonium; SPh<sub>3</sub><sup>+</sup>, triphenylsulfonium; t, tolerance factor; TMA, tetramethylammonium; TrMA, trimethylammonium.

## 2.10 Suggested Reading Resources

1. Wells, A.F., (2012). Structural Inorganic Chemistry. Oxford University Press.
2. West, A.R., (2014). Solid state chemistry and its applications. John Wiley and Sons.
3. Smart, L.E. and Moore, E.A., (2016). Solid state chemistry: an introduction. CRC press.
4. Chemistry class 12th PART 1 ncert, (2017)

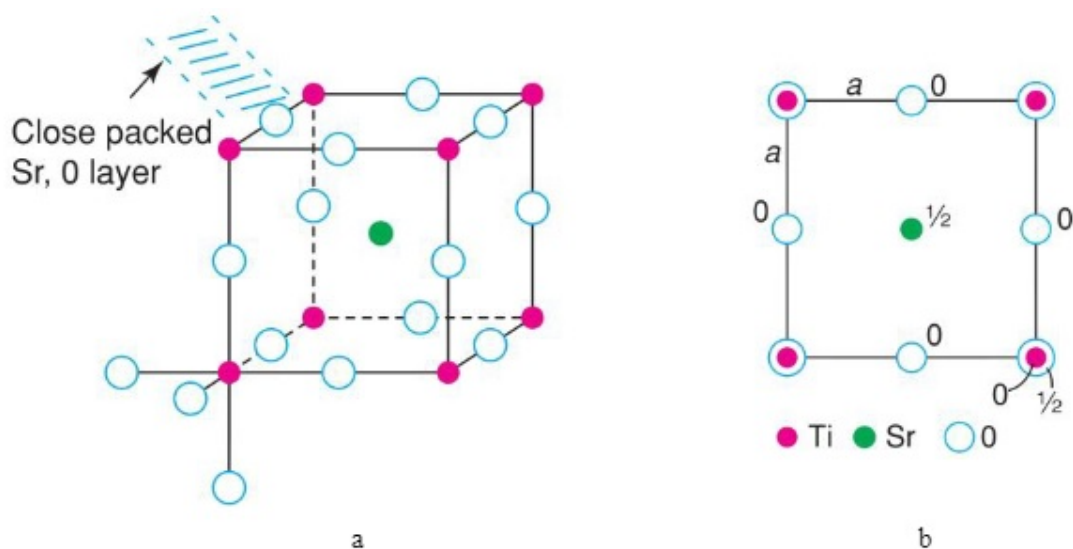
Figure 9. SrTiO<sub>3</sub> structure a) 3D-view; b) 2D-view.[2]

Figure 2.9:

Table 2.2: A summary of the chemical variabilities, crystal symmetries and physical properties of hybrid organic–inorganic perovskites

HOIPs	A-site	B-site	X-site	symmetry	Tolerance factor
Halides	MA and FA	Pn.Sn and Ce	Cl,Br,I <sup>-</sup>	orthorhombic trigonal Tetragonal Cubic	0.912-1.142
	MA PIP	K <sup>+</sup> /Bi <sup>3+</sup> K,Cs,and RB	Cl	cubic monoclinic Orthorhombic Trigonal	0.906-0.923 ) .922-1.037
Formates	Cs <sup>+</sup> ,K <sup>+</sup> ,NH <sub>4</sub> <sup>+</sup> ,MA, FA GUA,EA,DMA,AZE HIM and HAZ	Mg,Mn,Fe,Co Ni,Cu,Zn and Cd	(HCOO) <sup>-</sup>	Monoclinic Orthorhombic Trigonal Tetragonal	) .764 - 1.001 dielectricity
	HMA,DMA and EA	Na/Cr,Na/Al Na/Fe, K/Sc	(HCOO) <sup>-</sup>	Triclinic Trigonal	Ferroelasticity 0.897-1.040
Azides	MA,DMA and TMA	MN,cd and Co	N <sub>3</sub> <sup>-</sup>	Triclinic monoclinic Cubic	0.736-1.023
	TMA	Na/Cr, Na/Fe K/Fe,K/Cr			0.934-1.008
Dicyanamides	BTBA,BIEA,SPh <sub>3</sub> ,TMA	Mn,Fe,Co,Ni		Orthorhombic Tetragonal	1.142-1.166
Cyanides	HIM,dma.MA TMA,GUA	k/Fe,K/Co	CN <sup>-</sup>	Triclinic Monoclinic	0.840-1.031
	Borohydrides	MA	Ca	BH <sub>4</sub> <sup>-</sup>	cubic

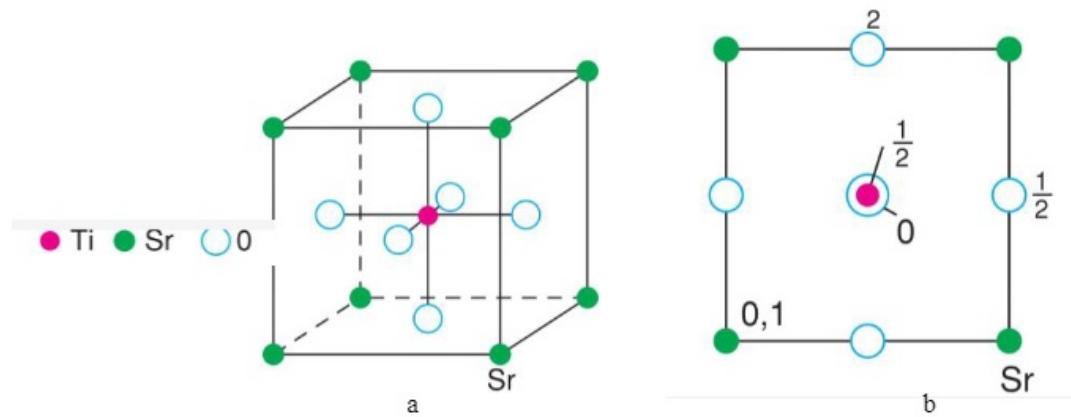


Figure 10. Translated view of  $\text{SrTiO}_3$  structure a) 3D-view; b) 2D-view.[2]

Figure 2.10: caption required

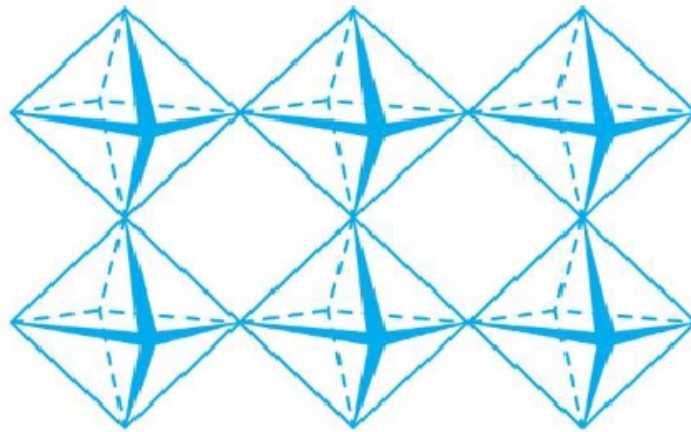


Figure 11.  $\text{SrTiO}_3$  as corner sharing octahedral framework structure.[2]

Figure 2.11: caption required here

5. Li, W., Wang, Z., Deschler, F., Gao, S., Friend, R.H. and Cheetham, A.K., (2017). Chemically diverse and multifunctional hybrid organic–inorganic perovskites. *Nature Reviews Materials*, 2(3), p.16099

## 2.11 $\text{A}_2\text{BO}_4$ -Layered Perovskite:

The  $\text{K}_2\text{NiF}_4$  structure: The  $\text{K}_2\text{NiF}_4$  structure may be regarded as alternating layers of perovskite and rock salt structures, as shown in Fig. 17. The formula  $\text{K}_2\text{NiF}_4$  could be written in expanded form as  $\text{KNiF}_3 \cdot \text{KF}$  to indicate the perovskite and rock salt components. The structure is body centred tetragonal with perovskite-like layers of octahedra centred at  $c=0$  and  $c=1/2$ .  $\text{K}^+$  ions lie at the interface between rock salt and perovskite blocks and have a coordination number of 9. The coordination number of K in rock salt would be 12 but the rock salt blocks are less than one unit cell thick and the K coordination in rock salt is interrupted by the atomic displacements that generate perovskite block.

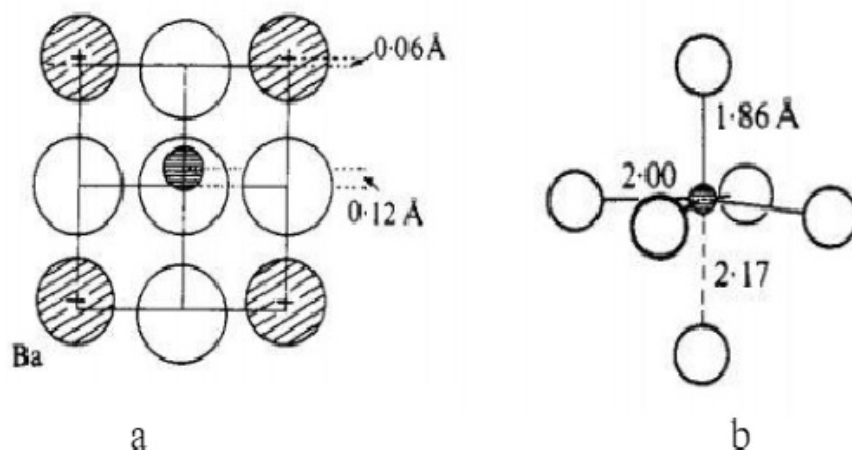


Figure 2.12: Distorted BaTiO<sub>3</sub> structure with  $t = 1.06$  (a) 2D-view B distortion in Ti octahedra[2]

## 2.12 Double Perovskite, $A_2BB'O_6$

In the double perovskite  $A_2B'B''O_6$  (where A is an alkaline-earth or rare-earth ion), the transition-metal sites (perovskite B-sites) are occupied alternately by different cations B' and B''. Sr<sub>2</sub>FeMoO<sub>6</sub> is one such example, as depicted in Fig. 18. Intervening oxygen bridges every B' and B'' atom pair, thus forming alternating B'O<sub>6</sub> and B''O<sub>6</sub> octahedra.

## 2.13 References

1. Wells, A.F., 2012. Structural inorganic chemistry. Oxford University Press.
2. West, A.R., 2014. Solid state chemistry and its applications. John Wiley and Sons.
3. Smart, L.E. and Moore, E.A., 2016. Solid state chemistry: an introduction. CRC press.
4. Chemistry class 12th PART 1 ncert, 2017.
5. Li, W., Wang, Z., Deschler, F., Gao, S., Friend, R.H. and Cheetham, A.K., 2017. Chemically diverse and multifunctional hybrid organic-inorganic perovskites. Nature Reviews Materials, 2(3), p.16099.
6. Kobayashi, K.I., Kimura, T., Sawada, H., Terakura, K. and Tokura, Y., 1998. Room-temperature magnetoresistance in an oxide material with an ordered double-perovskite structure. Nature, 395(6703), p.677

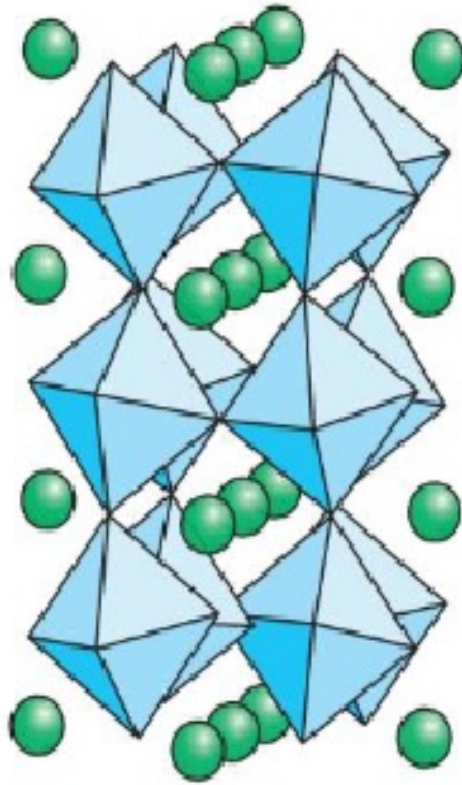


Figure 2.13: GdFeO<sub>3</sub> structure with  $0.85 < t < 0.90$  showing tilting of the BO<sub>6</sub> octahedra.[2]

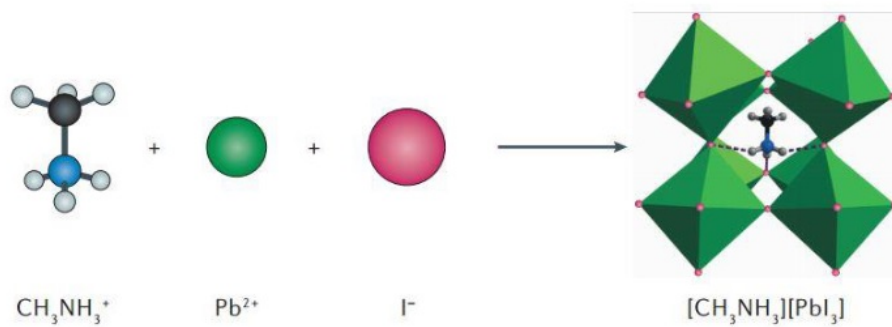


Figure 14. HOIP with an organic cation at the A-site, MAPbI<sub>3</sub> (orthorhombic, MA = methylammonium) [5]

Figure 2.14:



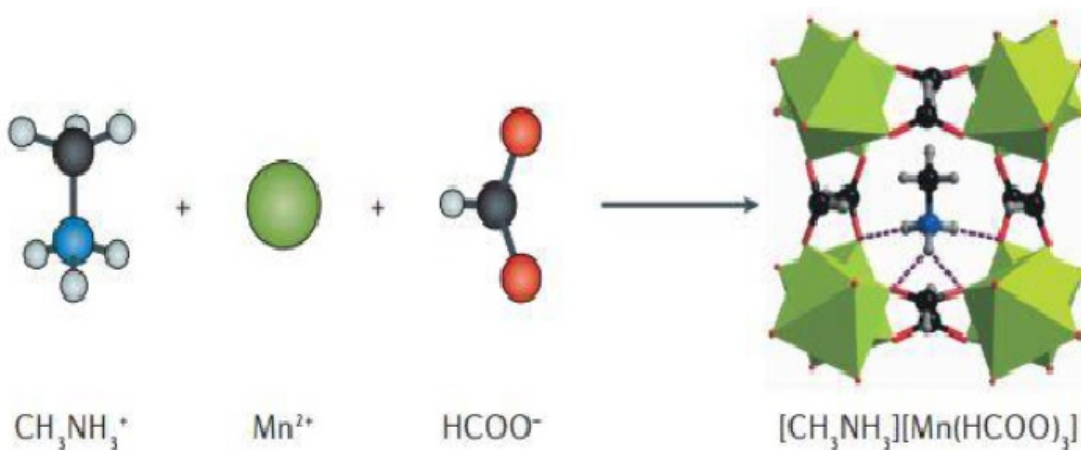


Figure 2.15: HOIP with an organic cation at the A-site and an organic anion at the X-site (a metal–organic framework perovskite),  $[\text{MA}][\text{Mn}(\text{HCOO})_3]$  (orthorhombic). [5]

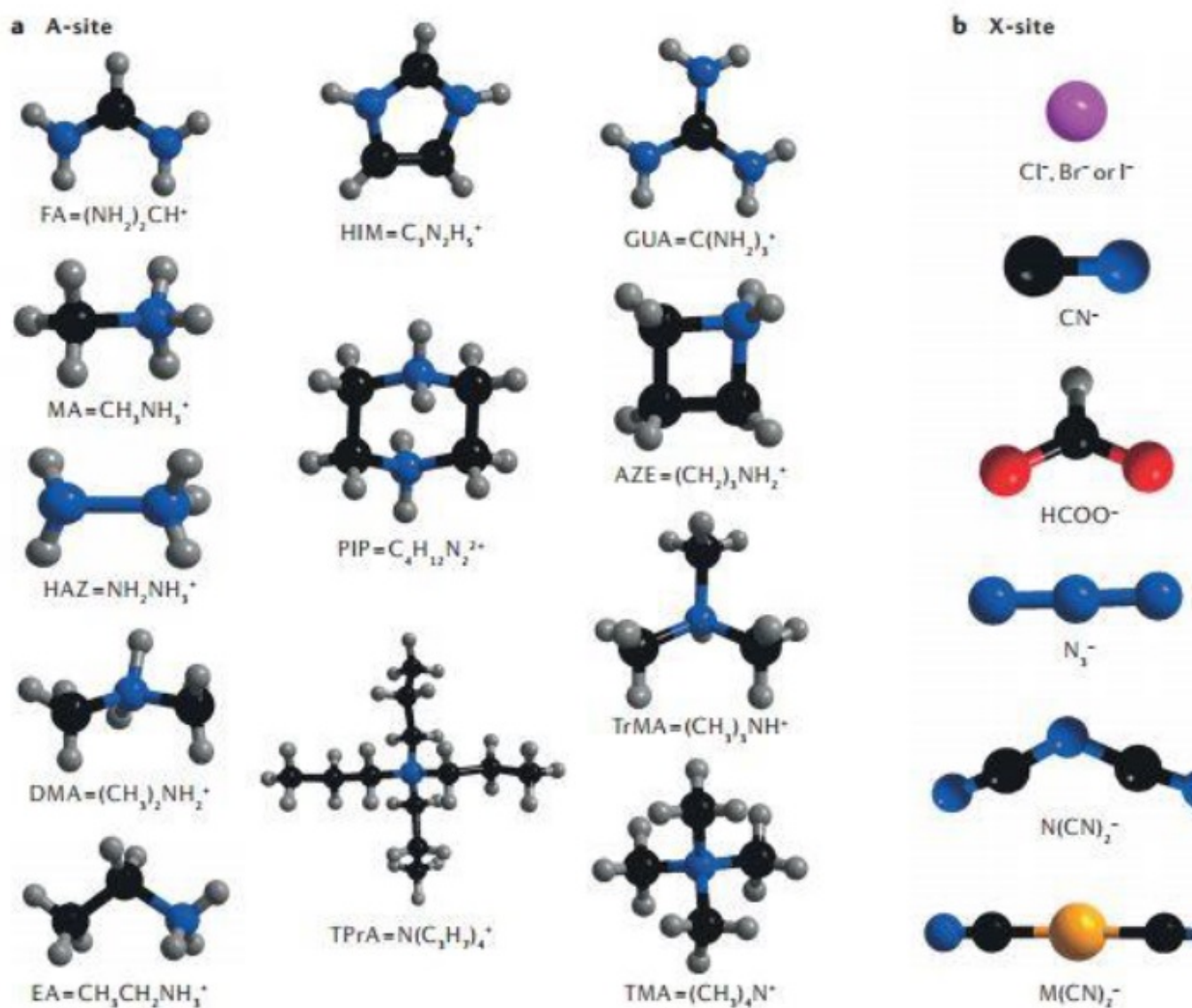


Figure 2.16: a) The structures of a selection of possible A-site cations used in (HOIPs); b) The structures of a selection of possible X-site anions used in HOIPs. [5] .

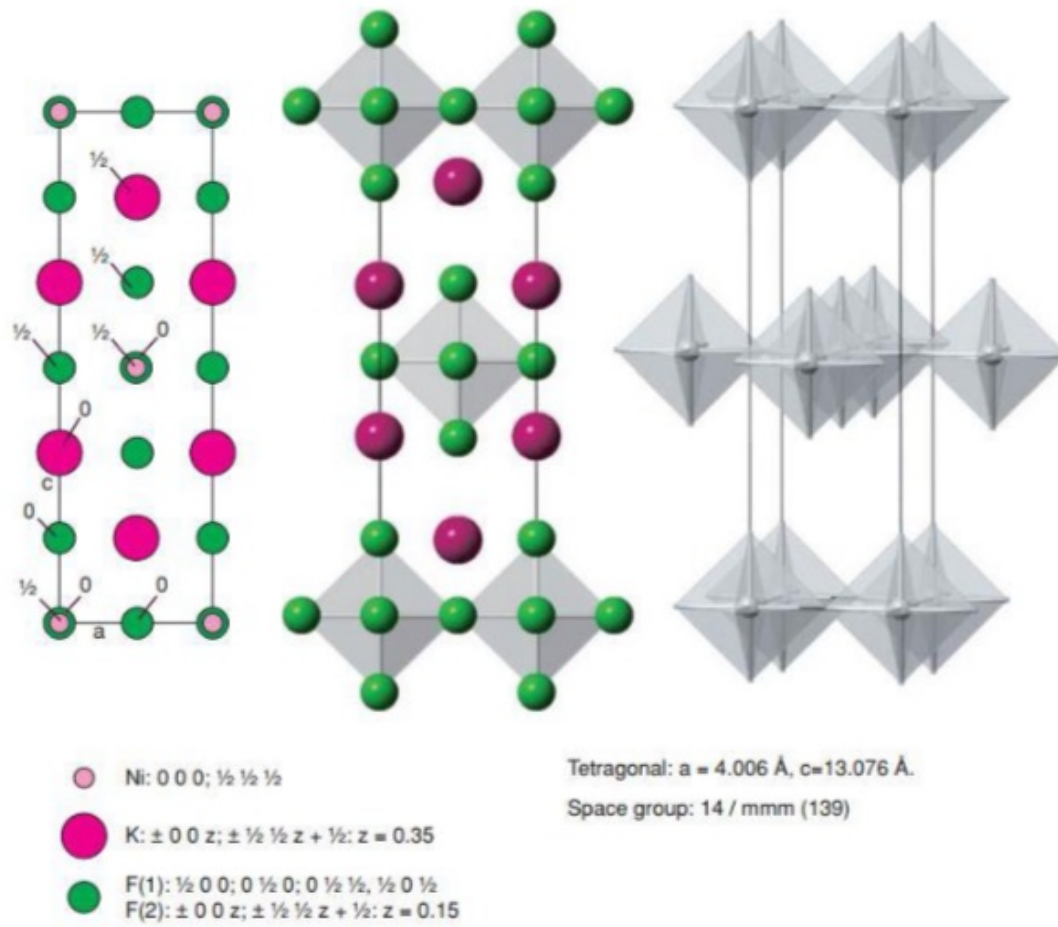


Figure 2.17:  $A_2BO_4$ -Layered Perovskite: The  $K_2NiF_4$  structure.[2]



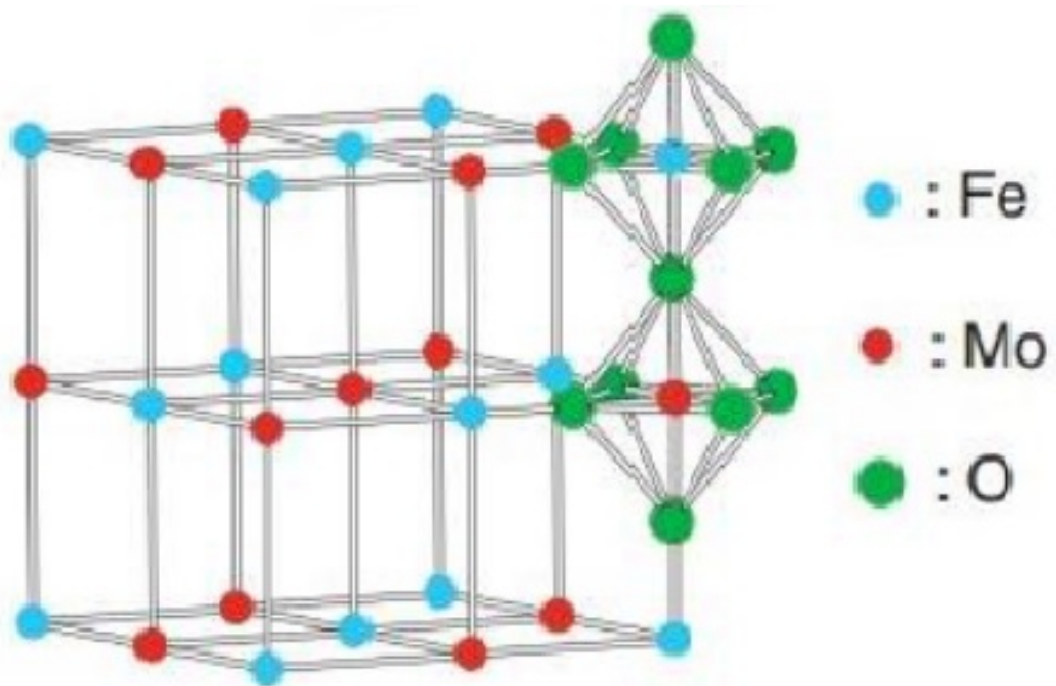


Figure 2.18: double perovskite  $\text{A}_2\text{BB}'\text{O}_6$  : The  $\text{Sr}_2\text{FeMoO}_6$  structure.[6]



# Chapter 3

## APPLICATIONS OF PEROVSKITES

### 3.1 Perovskites in Magnetic Devices

Transition metal oxides of the perovskite  $ABO_3$  materials have been an enticed area of material research for several decades in theoretical as well as application points of view owing to their intriguing physical properties such as superconductivity, multiferroicity, charge transfer, spin-dependent transport and colossal magnetoresistance along with their potential application in information storage, batteries, fuel cells spintronics and more [1-4]. Oxide-based heterostructures (crystallising in  $ABO_3$  perovskite structure) opened receptive scope to a broader range of functionalities realised by changes in electron-lattice correlation modified by structural distortion, octahedral tilt, temperature, pressure and also as a consequent interplay between charge, orbital, spin and lattice degrees of freedom [5-10]. We present in this chapter a wide range of applications of perovskites from the magnetic device application point of view with a highlight on a fundamental understanding of the electronic and magnetic structure of the perovskite materials. We hope that the chapter will stimulate more interest in perovskites and help readers better understand some important scientific concepts which explain how perovskites took its place as promising candidate in magnetic device application.

### 3.2 Electronic Structure of Perovskites

To begin with, it is essential to understand the electronic structure of perovskites for better understanding of their application in magnetic devices. In the  $ABO_3$  structure, the B site cation is responsible for numerous exciting phenomena as a consequence of strong electron interactions between the partially filled d-orbitals in the B site cations. Regardless of the specific structure variants in the perovskite structure, the B site cation is always surrounded by six nearest neighbour of oxygen anions. As one would expect, due to the Coulomb repulsion between the 'd' orbital electrons and the surrounding charges from oxygen, the energy of the d-orbital increases as the oxygen anions approach the B site cations. Thus, the crystal environment of such oxygen octahedra breaks the five-fold degenerate d-orbitals into two high energy  $e_g$  orbitals and three low energy  $t_{2g}$  orbitals. The deformation of the octahedral structures due to internal (Jahn-Teller distortion) or external (e.g. epitaxial strain) perturbation can lift the degeneracies between the  $e_g$  and  $t_{2g}$  orbitals further to reach an energy occupation configuration.

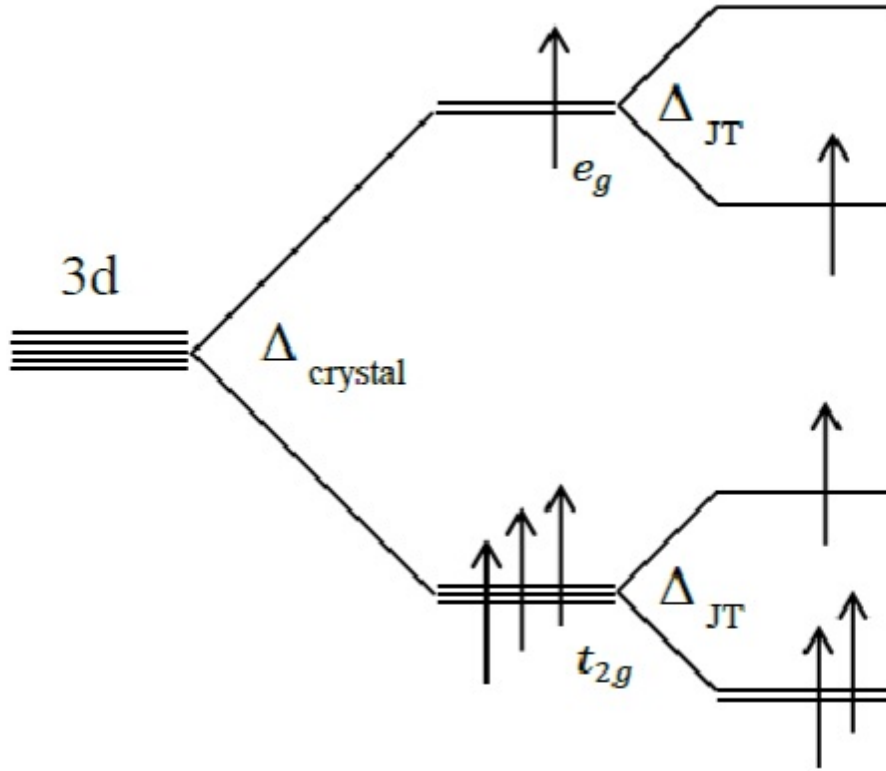


Figure 3.1: Schematic representation of crystal field splitting of five-fold degenerate atomic 3d-orbitals into  $d$  and  $e$  levels, further splitting due to Jahn-Teller (JT) distortions.

### 3.3 Perovskites in Magnetocaloric Effect Based Magnetic Refrigerators

Magnetic refrigeration is a cooling technology based on the magneto-caloric effect. This technique can be used to attain extremely low temperatures, as well as the ranges used in conventional refrigerators. The magneto-caloric effect (MCE) is an intrinsic property of all magnetic materials and is induced through the coupling of a spin system with a magnetic field. When a magnetic field is applied adiabatically to a magnetic material, the spins in the material are aligned parallel to the field. Due to the reduced magnetic entropy, the material warms up to offset the lost magnetic entropy through an increase of the lattice entropy. Upon removal of the magnetic field, the ensuing spin randomisation results in a rise of the magnetic entropy and a decrease of the lattice entropy (i.e. a drop in temperature). The magnetic refrigeration Carnot cycle cooling efficiency is 30-60% compared to 5-10% gas-compression refrigeration. Also, magnetic refrigeration is environmentally friendly as it does not use ozone-depleting or global warming gases. According to the Curie-Weiss law, ferromagnetic materials with a large effective Bohr magneton-number  $P$  ( $P = g[J(J+1)]^{1/2}$ , where  $g$  is the  $g$  factor, and  $J$  is the total angular momentum quantum number) are expected to have a substantial magnetic entropy change at the Curie temperature  $T_C$ . Given that, researchers of the previous studies mainly concentrated on intermetallic compounds and the alloys of rare earth metals with high  $J$ . In 1995 and 1996, anomalous thermal expansions were observed in perovskite-type ferromagnetic oxides at their Curie temperatures; some of them exhibited a sharp change of magnetisation and a discontinuous volume variation at the field. Due to the reduced magnetic entropy, the material warms up to offset the lost magnetic entropy through an increase of the lattice entropy. Upon removal of the magnetic field, the ensuing spin randomization results in a rise

of the magnetic entropy and a decrease of the lattice entropy (i.e. a drop-in temperature). The magnetic refrigeration Carnot cycle cooling efficiency is 30-60% compared to 5-10% gas compression refrigeration. Also, magnetic refrigeration is environmentally friendly as it does not use ozone-depleting or global warming gases. According to the Curie–Weiss law, ferromagnetic materials with a large effective Bohr magneton number  $P$  ( $P = g[J(J + 1)]^{1/2}$ , where  $g$  is the  $g$  factor, and  $J$  is the total angular momentum quantum number) are expected to have a substantial magnetic entropy change at the Curie temperature. Given that, researchers of the previous studies mainly concentrated on intermetallic compounds and the alloys of rare earth metals with high  $J$ . In 1995 and 1996, anomalous thermal expansions were observed in perovskite-type ferromagnetic oxides at their Curie temperatures; some of them exhibited a sharp change of magnetisation and a discontinuous volume variation at the ferromagnetic transition. The simultaneous structural and magnetic changes at  $T_C$  could have a strong influence on the magnetic entropy change [11]. Compared with the rare earth metals and their alloys, the perovskite type oxides exhibit a considerably smaller magnetic hysteresis, higher chemical stability, and a higher electrical resistivity that favours a lower value of eddy-current heating. In other words, the perovskite-type oxides appear to be more suitable candidates for magnetic refrigeration at high temperatures, especially near room temperature.

### 3.4 Perovskites in Spintronics

Spintronics is a conventional digital electronic system conveys a binary signal (think 1s and 0s) through pulses of electrons carried through a conductive wire. Spintronics can convey additional information via another characteristic of electrons, their spin direction (think up or down). Spin is related to magnetism. So spintronics uses magnetism to align electrons of a particular spin, or "inject" spin into a system. Because of heavy lead atoms in perovskite, physicists predicted that the mineral might possess strong s "inject" spin into a system. Because of heavy lead atoms in perovskite, physicists predicted that the mineral might possess strong spin-orbit coupling. In a 2017 paper, Vardeny and Sarah Li showed that a class of perovskites called organic-inorganic hybrid perovskites do indeed possess large spin-orbit coupling. Also, the lifetime of spin injected into the hybrid materials lasted a relatively long time. Both results suggested that this kind of hybrid perovskite held promise as a spintronics material. The next step, which Vardeny and Wang accomplished in their recent work, was to incorporate hybrid perovskite into spintronic devices.

The first device is a spintronic light-emitting diode or LED. The semiconductor in a traditional LED contains electrons and holes, places in atoms where electrons should be but are not. When electrons flow through the diode, they fill the holes and emit light. Wang says that a spintronic LED works much the same way, but with a magnetic electrode, and with electron holes polarised to accommodate electrons of a particular spin. The LED lit up with circularly polarised electroluminescence, Wang says, showing that the magnetic electrode successfully transferred spin-polarised electrons into the material. "It is not self-evident that if you put a semiconductor and a ferromagnet together, you get a spin injection," Vardeny adds. "You have to prove it.

Moreover, they proved it. "The second device is a spin valve. Similar devices already exist and are used in devices such as computer hard drives. In a spin valve, an external magnetic field flips the polarity of magnetic materials in the valve between an open, low-resistance state and a closed, high-resistance state. Wang and Vardeny's spin valve do more. With hybrid perovskite as the device material, the researchers can inject spin into the device and then cause the spin to precess, or wobble, within the device using magnetic manipulation. That is a big

deal, the researchers say. "You can develop spintronics that are not only useful for recording information and data storage, but also calculation," Wang says. "That was an initial goal for the people who started the field of spintronics. and that is what we are still working on. "Taken together, these experiments show that perovskites works as a spintronic semiconductor. The ultimate goal of a spin-based transistor is still several steps away, but this study lays important groundwork for the path ahead. "What we have done is to prove that what people thought was possible with perovskite happens," Vardeny says. "That is a big step.

### 3.5 Perovskites in Data Storage System

With the advance of technology, the need for storage systems with higher density and efficiency increased, and this also requires materials with tunable magnetic properties in order to read and write data over them. EPFL scientists have developed a perovskite material whose magnetic order can be rapidly changed without disrupting it due to heating. The work, which describes the first ever magnetic photo-conductor, is published in Nature Communications. Magnetism in material arises from the interactions of localised and moving electrons of the material; in a way, it is the result of competition between different movements of electrons. This means that the resulting magnetic state is wired in the material and it cannot be reversed without changing the structure of electrons in the material's chemistry or crystal structure. However, an easy way to modify magnetic properties would be an enormous advantage in many applications, such as magnetic data storage. The new material that the EPFL scientists developed the first magnetic photo-conductor. This new crystal structure combines the advantages of both ferromagnets, whose magnetic moments are aligned in a well-defined order, and photo-conductors, where light illumination generates high density free conduction electrons. The combination of the two properties produced an entirely new phenomenon: the "melting" of magnetisation by photo-electrons, which are electrons that are emitted from a material when light hits it. In the new perovskite material, a simple red LED weaker than a laser pointer is enough to disrupt, or "melt" the material's magnetic order and generate a high density of traveling electrons which can be freely and continuously tuned by changing the light intensity. The time scale for shifting the magnetic in this material is very fast, virtually needing only quadrillionths of a second. Though still experimental, all these properties mean that the new material can be used to build the next generation of memory-storage systems, featuring higher capacities with low energy demands.

### 3.6 References

1. A. Ohtomo, H. Y. Hwang . A high-mobility electron gas at the LaAlO<sub>3</sub>/SrTiO<sub>3</sub> heterointerface. *Nature* 427, 423–426 (2004).
2. M. N. Iliev, P. Padhan, and A. Gupta. Temperature-dependent Raman study of multiferroic Bi<sub>2</sub>NiMnO<sub>6</sub> thin films. *Phys.Rev.B* 77, 172303 (2008).
3. Kai Lv, H. P. Zhu, W. Q. Zou, F. M. Zhang, and X. S. Wu, Charge transfer and orbital-reconstruction in the (La<sub>2</sub>/3Sr<sub>1</sub>/3MnO<sub>3</sub>)<sub>m</sub>/(SrRuO<sub>3</sub>)<sub>n</sub> Superlattices. *J. Appl. Phys.* 117, 185305(2015).
4. Aamir Minhas Khan, Arif Mumtaz, Syed Khurshid Hasanain, Anwar Ul Haq. Low temperature magnetoresistive effects and coulomb blockade in La<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> nanoparticles synthesis by auto-Ignition method. *Natural Science*. Vol.3, No.6, 496-501 (2011).
5. Elbio Dagotto. When Oxides Meet Face to Face *Science* 318 (5853), 1076-1077 (2007) 6.

- Nico Homonnay, Kerry J. Oshea, Christian Eisenschmidt, Martin Wahler, Donald A. MacLaren and Georg Schmidt. Interface Reactions in LSMO Metal Hybrid Structures. *Appl Mater. Interfaces*. **7**, 22196-22202 (2015).
7. B. C. Behera, A. V. Ravindra, P. Padhan, and W. Prellier. Raman spectra and magnetization of all-ferromagnetic superlattices grown on (110) oriented SrTiO<sub>3</sub>. *Appl. Phys. Lett.* **104**, 092406(2014).
8. P. Padhan, and W. Prellier. Size effect on magnetic coupling in all-ferromagnetic superlattices. *Appl. Phys. Lett.* **99**, 263108 (2011).
9. Sujit Das, Andreas Herklotz, Eckhard Pippel, Er Jia Guo, Diana Rata and Kathrin.D., Strain dependence of antiferromagnetic interface coupling in La<sub>0.70</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>/SrRuO<sub>3</sub> superlattices, *Phys.Rev.B*. **91**, 134405 (2015).
10. B.C. Behera, P.Padhan , W.Prellier . Influence of substrate in all-ferromagnetic superlattices. *J Magn Magn Mater.* 22-27 388(2015)
11. Zhong Wei, Au Chak-Tong, , and Du You-Wei . Review of magnetocaloric effect in perovskite type oxides. *Chin. Phys. B* Vol. **22**, No. **5** ,057501(2013).





# Chapter 4

## HYBRID ORGANIC INORGANIC PEROVSKITES - AN INTRODUCTION

### 4.1 Introduction

The desire to surpass the efficiency of silicon in converting photon energy to electricity and thereby other useful chemicals has been pushing the scientists and engineers to find alternate materials not only to replace silicon (possibly due to cost considerations and processing methods) but also make the process of manufacture of these new materials in an easier way as compared to manufacture of single crystal silicon. In this exercise, lasting for more than 5 to 6 decades a new material has emerged in 2009, since then there is sudden raise in efficiency of perovskite based solar cells from 3.8% to nearly 22% which has stunned the photovoltaic community. This situation warrants attention not only from the point of view of increased efficiency but also the possibility of a number of new systems emerging due to the fact that a number of possibilities exist in the variation of composition in  $ABX_3$  perovskite structure. Research on solar cell possibly started in 1839 with Alexandre Edmond Becquerel. In 1873, photo-conductivity was discovered in selenium by Willoughby Smith an English engineer. First solar cell was made by American inventor Charles Fritts based on selenium. In 1940, Bell laboratories started research on semiconductor based solar cells and patented a cell with 1% efficiency. In 1954, Bell laboratories demonstrated the first practical silicon based solar cells. In the similar way, the brief history of organic inorganic perovskites traces back to 1893. H.L. Wells first synthesized alkali metal tin and lead halides. In 1958, the chemical structure of perovskite caesium lead halide was determined by Christian Mueller. In 1978, Dieter Weber replaced trimethyl ammonium ion in the caesium lead halide to form a class of compounds called Hybrid Organic Inorganic Perovskites (HOIP). The optical and other properties of these new generation compounds have been examined since the last two decades and their application in solar cells started in 2009. The growth in solar cell efficiency is pictorially shown in Fig.1. This figure also gives the progress in efficiency of other solar cell materials like crystalline silicon, CdTe, Dye sensitized solar cells and quantum dots. Compared to other well-known Solar cell materials the efficiency of organic inorganic solar cells has reached a value of around 23% in a short span of less than a decade. The scope of generating newer materials for solar cell application among this class of organic inorganic perovskites appears to be great. This is demonstrated by Gregor Kiealich et al. [2]. They have used the concept of tolerance factor (conventionally known as Goldschmidt's tolerance factor) and applied to the permutations of 14 different protonated amines 8 different anionic species and 21 divalent metal ions generated 2352 tolerance factor (TF) values, out of these 742 had tolerance factor values in the range 0.8 to 1 (the limits of perovskite structure) out of which 140 are known materials and the remaining 562 are organic anion based. This study with limited number of organic cations shows that

there is still scope of finding suitable materials for solar cell application. This limited discussion on the possibility of generating many unknown materials with perovskite structure speaks volumes on the feasibility of generating new solar cell materials with the required efficiency in the near future.

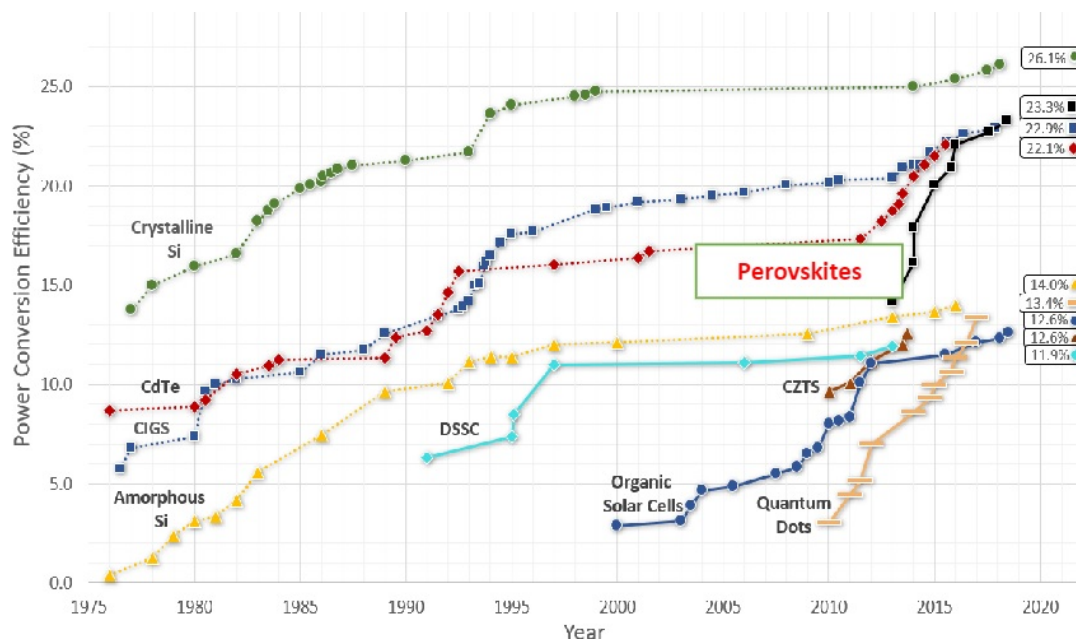


Figure 4.1: Values of the efficiency versus time plot for various (crystalline Silicon, CdTe, DSSC, organic solar cells). Perovskite solar cells have increased in power conversion efficiency at a phenomenal rate compared to other types of photovoltaics. [reproduced from Ref [1].

Fig.2 Illustrates the rapid increase in the efficiency of perovskite solar cells. The increase achieved in the past decade is remarkable. The cells have already achieved documented efficiencies of the order of greater than 23%, which represents an unprecedented rate of progress compared to any other solar cell technology. For comparison the rate of increase of efficiency for other typical solar cells are also shown for a chosen typical solar cell. OPV stands for organic photovoltaics; DSSC means dye-sensitized solar cell; A-Si stands for amorphous Si solar cell; Efficiency denotes solar to electrical power conversion efficiency of the best cells at that time [reproduced from ref.7].

In the synthesis of HOIP, the pioneering work was done by Schmidt et al [3]. This team synthesized HOIP by injecting methyl ammonium bromide and lead bromide solutions into a preheated reaction medium oleic acid and octyl ammonium bromide dissolved in octadecene. The particles are Perovskites precipitated by adding acetone. Zhang et al. [4] have developed a ligand assisted re-precipitation approach for preparing methylammonium lead halide nanoparticles. The synthesis procedure involves step-wise injection of a solution of the precursors in DMF and precipitation in toluene. Fig.1b Typical solar cell efficiency for chosen systems with respect to the period. [reproduced from ref.7]. Vapour assisted solution process consists of crystallization of metal halide coated substrate which is spin coated before hand into a methyl ammonium iodide vapour filled environment. This synthesis procedure was adopted to get a material which originally gave an efficiency of 12.1% [5]. Though in the initial stages of the precipitation of the precursors, the perovskite framework is formed, its growth and the conditions under which various architectures are evolved and the role of impurities in the formation of nucleus and growth are not well documented in literature [6]. Even though low temperature

## Evolution of hybrid I-O Perovskite solar cells

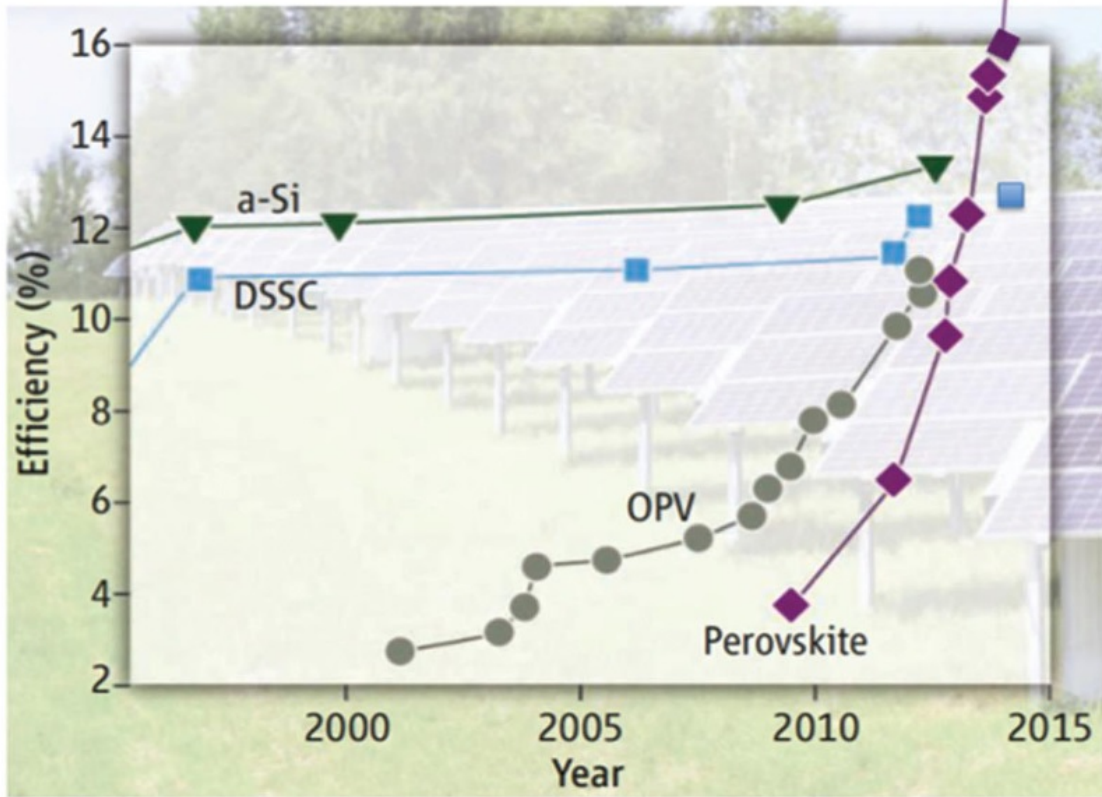


Figure 4.2: Fig.1b Typical solar cell efficiency for chosen systems with respect to the period. [reproduced from reference 7]

solution phase methods are applicable for preparation of these materials, their stability and optical properties are still to be improved and it is hoped considerable progress in these directions will take place in the near future.

Table 1. Transport characteristics of HOIPs and their comparisons with those characteristics of other semiconductors

Table 4.1: Material characteristics of perovskite and semiconductor materials

Material	Diffusion length ( $\mu\text{m}$ )	Carrier life time ( $\mu\text{s}$ )	Mobility ( $\text{cm}^2\text{V}^{-1}$ )
$\text{CH}_3\text{NH}_3\text{PbI}_3$ (Polycrystalline film)	0.01-1	0.01-1	1-10
$\text{CH}_3\text{NH}_3\text{PbI}_3$ (Single crystal)	2-8	0.5-1	24-105
$\text{CH}_3\text{NH}_3\text{PbBr}_3$ (Polycrystalline film)	0.3-1	0.05-0.16	30
$\text{CH}_3\text{NH}_3\text{PbBr}_3$ (Single crystal)	3-17	0.3-1	24-115
Silicon ( $e^-h^+$ )	1-600	1000	1450-500
GaAs ( $e^-h^+$ )	7-1.6	0.1-1.0	8000-400

HOIPs are softer mechanically as compared to other efficient solar cell materials. What does this imply? HOIPs are susceptible for many facile phase transitions (in this sense these are dynamic materials) inducing migration of intrinsic and extrinsic ionic species. These fluctuations and long-range ionic motions have strong impact on charge transport and optical properties.

Table 4.2: Structural phase transitions for commonly employed hybrid perovskites

Composition	Phase	Temp (K)	Structure	Space group	Band gap (eV)	Volume (Å <sup>3</sup> )
MAPbI <sub>3</sub>	Alpha	400	Tetragonal	P4mm	1.51-1.55	251.6
	Beta	293	Tetragonal	I4m	-	900
	Gamma	162-172	Orthorhombic	Pna2	-	959.6
MAPbCl <sub>3</sub>	Alpha	178.8	Cubic Pm3m	-	-	182.2
	Beta	172.9-178.8	Tetragonal	P4/mmm	-	180
	Gamma	172.9	Orthorhombic	P222	-	375
MAPbBr <sub>3</sub>	Alpha	236.9	Cubic Pm3m	-	-	286.3
	Beta	155.1	Tetragonal	I4/m	-	819.4
	Gamma	144.5	Tetragonal	P4/mmm	-	811.1
MASnI <sub>3</sub>	Alpha	293	Tetragonal	P4mm	-	241.9
	Beta	200	Tetragonal	I4/m	-	952.1
FAPbI <sub>3</sub>	Alpha	293	Tetragonal	P2m	1.43-1.48	748.9
	Beta	150	Tetragonal	P3	-	2988.4
FASnI <sub>3</sub>	Alpha	340	Orthorhombic	Amm2	-	509.03
	Beta	180	Orthorhombic	Imm2	-	1959.2

Perovskite structure is usually adopted by ABO<sub>3</sub> types of oxide materials. Hybrid organic inorganic perovskites with the composition ABX<sub>3</sub> where A and B are mono and bivalent cations and X can be monovalent anion and A cation is an organic component.

## 4.2 References

1. <https://www.ossila.com/pages/perovskites-and-perovskite-solar-cells-an-introduction>.
2. Gregir Kieslich, Shijing Sun and A.K.Cheetham, An extended Tolerance factor approach-skites, organic-inorganic perovskites, Chem.Sci., 6, 3430 (2015).
3. Schmidt L.C., Pretegas, A., Gonzalez-Crrero,S., Malinkiewicz, re O., Agouram,S.,Espallargas,G.M., Bolin,H.J., Galian,B.E., Perez-Prieto,J., J.Am.Chem.Soc., 136, 850(2014).
4. Zhang,F., Zhong,H., Chen,X.C., Wu,H., Huang,J., Han,B., Zou,Y., Dong, ACS Nano,9,4533 (2015).
5. Thomas, M. Brenner, David A.Egger, Lecor Kronik, Cary Hodes, and David Cahen, HybridOrganic-Inorganic perovskites low-cost semiconductors with intriguing charge transport-properties, Nature reviews,1, 1-6 (2016).
6. Qi Chen, Nicholas De Marco, Yang (Michael) Yang, Tze-Bin Song, Z.Hong, Chun ChaoChen, H.Zhao, Z.Hong, H.Zhou, Yang Yang, Under the spotlight: The organic-inorganichybrid halide perovskite for optoelectronic applications, Nano Today, 10,355 (2015)
7. Joseph Berry , Tonio Buonassisi , David A. Egger , Gary Hodes , Leeor Kronik , Yueh-LinLoo, Igor Lubomirsky Seth R. Marder , Yitzhak Mastai , Joel S. Miller , David B. Mitzi, Yaron Paz, Andrew M. Rappe , Ilan Riess , Boris Rybtchinski , Oscar Stafsudd , VladanStevanovic , Michael F. Toney , David Zitoun , Antoine Kahn , David Ginley ,and DavidCahen, Hybrid Organic-Inorganic Perovskites (HOIPs): Opportunities and Challenges,Adv. Mater. 2015, 27, 5102-5112

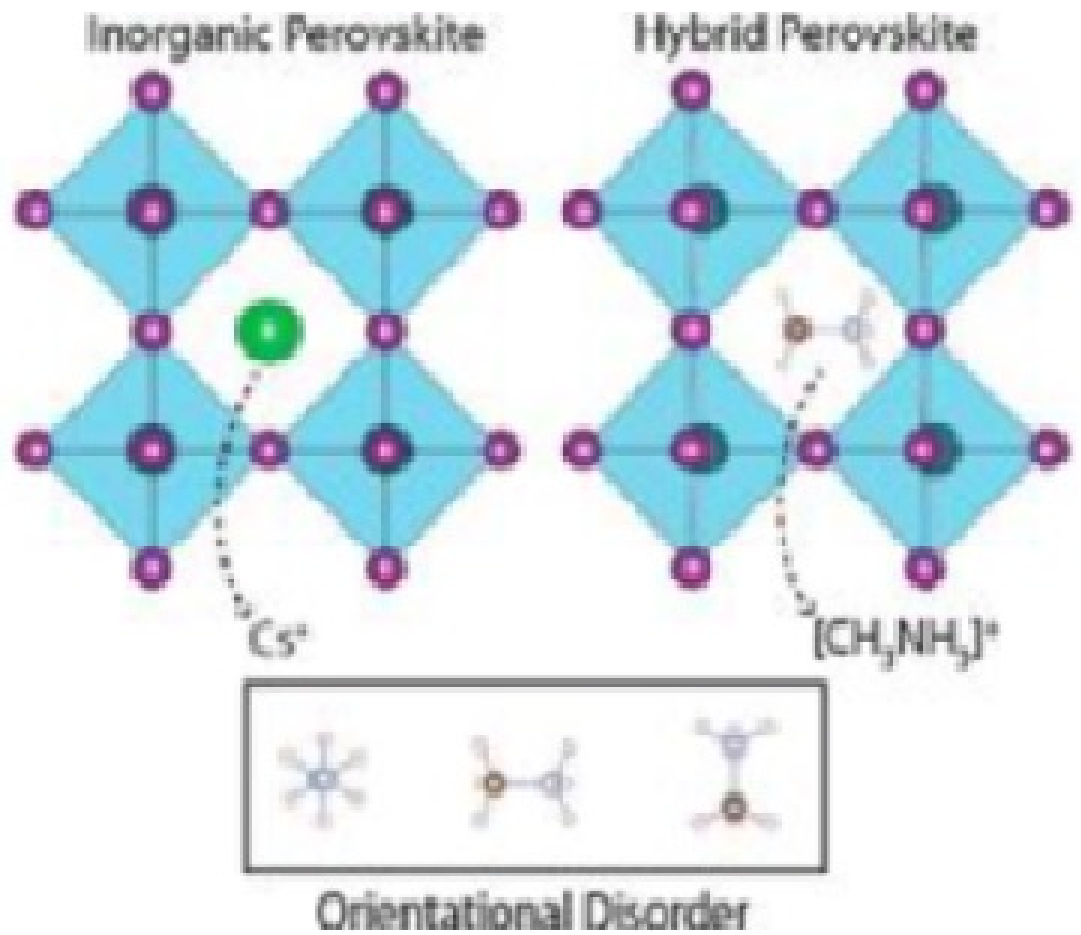


Figure 4.3: Orientational disorder associated with the non-spherically symmetric organicmethylammonium [(CH<sub>3</sub>NH<sub>3</sub>)] cation as compared to the spherically symmetric inorganic cation[Reproduced from reference 6]



# Chapter 5

## PERSPECTIVES ON PEROVSKITES

### 5.1 Perovskite Solar Cells

The science of perovskite materials is at crossroads since, in many applications like solar cells, they are competing with the already established high-performance materials. The current situation on these materials is reflected from the number of high impact scientific publications in various journals and also the establishment of the perovskite-info weekly newsletter. This situation is mainly due to the possibility of generating innumerable compositions with this structure. This situation today warrants a selection based on thousands (even millions) of possibilities, and hence one has to resort to some predictions based on computer-based screening of materials. This is reflected in the recent publications on this topic [1]. Designing new functional materials has always been a challenge since the conventional methods are ineffective when one has to screen thousands of potential materials [2,3].

There are empirical methods (like tolerance factor) that have been commonly employed to predict the formation of the perovskite phase. However, it must be stated that there are limitations to this method, especially for hybrid systems. This aspect has been dealt with in earlier chapters. The synthesis methodologies adopted for forming perovskite phases are simple and straight forward like solid-state reaction, complex decomposition or co-precipitation, and so on. These methods generally yield the perovskite phase as identified by the X-ray diffraction method.

The versatility of perovskites arises from the geometry of the crystal structure and the ionic radii of the constituent ions. The electronic configuration of the various ions is mainly responsible for the observed electrical and magnetic and dielectric property of the perovskite systems. One of the applications where perovskites are threatening to replace almost all other alternatives is the exploitation of their opto-electronic property, and hence, they are today considered as the materials for solar cells. The progress in this application of these materials has been dealt with in the earlier chapters. The rapid progress in this field is again traced in the following figure

Despite this rapid development, some critical factors appear to restrict this unusually rapid development of perovskite-based solar cells [4,5]. These can be listed as follows:

- The stability especially of the organic lead halide perovskites is greatly affected by environmental factors (like humidity, temperature, and radiation), which lead to the low stability of the devices and the great difficulties in encapsulating cells. To specify the exact composition of the device and also to package the layers for the charge transport will be necessary for the practical application of these devices.
- The hole transporting material employed in perovskite-based solar cells is expensive, and its synthesis procedure is complicated. Therefore, it is necessary to find alternate hole transport materials to adapt to the commercial applications of perovskite solar cells

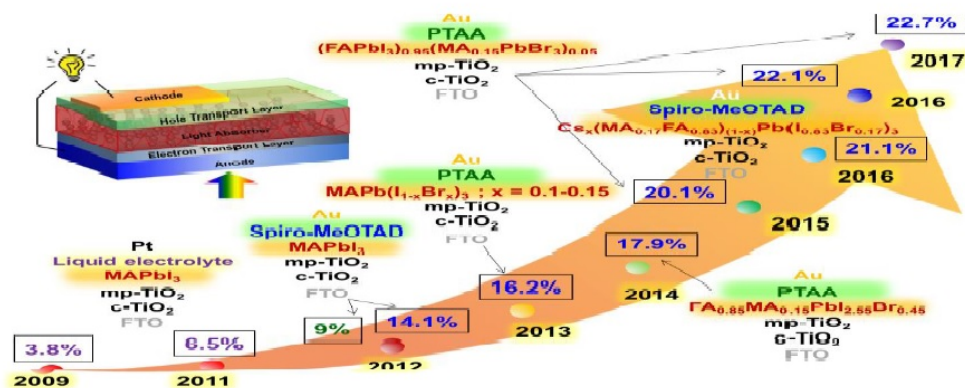


Figure 5.1: The graphical representation of the year-wise evolution of the efficiency of perovskite based solar cells. The figures in blue are the certified efficiencies by NREL. [Figure reproduced from reference 6]

- Technologically obtaining large area perovskite films with the available traditional methods is difficult. There is a need to improve these deposition methods for commercial production in the future.
- The elements involved (especially Pb) employed in perovskite solar cells is toxic, which will come in the way of industrial production and promotion of this technology. Various alternatives have been proposed and being tested including double perovskites [7,8,9]
- The understanding of the microscopic mechanism of perovskite solar cells has not reached the desired levels. This aspect has to be carefully looked into so that further improvements in performance and new materials can be formulated.

The progress in the value of the efficiency of perovskite solar cells is impressive, but the issue of instability has attracted enormous attention. For the commercialisation of perovskite-based solar cells, instability of the fabricated device is the main barrier that has to be surmounted. There is a considerable improvement in the stability of perovskites. Still, it has to be improved considerably. Structural design, charge transport materials, encapsulation methods have to be improved [10,11]. The replacing the poisonous lead has been attempted by applying Goldschmidt's rule and also quantum mechanical calculations and this methodology has been used for the development of photovoltaics. It is interesting to pay attention to the opto-electronic properties of the lead-free materials to provide environmentally friendly devices. This methodology has to be improved further [12]. The factors namely low cost, large area, high throughput, high solar-to-energy, reproducibility long lifetime and toxicity have to be optimized for these photovoltaic devices to industrial scale applications. [13]. There are various aspects wherein the improvements are essential, and leading experts have discussed these in recent times. [14-18]. These can be identified as thermal stability, grain boundary defects, the stoichiometry of the phases, the hysteresis of the materials, and also moisture stability, and all these aspects have to



be carefully overcome so that commercialization of the technology will prove fruitful. There is considerable progress in identifying the cause of these shortcomings, and how to overcome them but still more research efforts have to be expanded in order to make these materials suitable for commercial applications.



# Bibliography

- [1] Gregir Kieslich, Shijing Sun and A.K.Cheetham, An extended Tolerance factor approach for organic-inorganic perovskites. *Chem. Sci.*, 6, 3430 (2015).
- [2] Shuaihua Lu, Qionghua Zhou, Yixin Ouyang, Yilv Guo, Qiang Li, and Jinlan Wang, Accelerated discovery of stable lead-free hybrid organic-inorganic perovskites via machine learning, *Nat. Commun.*, 9, 3405 (2018).
- [3] Chiho Kin, Tran Doan Huan, Sridevi Krishnan and Rampi Ramprasad, A hybrid organic-inorganic perovskite dataset, *Sci. Data*, 4, 170057 (2017).
- [4] Berry J, Buonassisi T, Egger DA, Hodes G, Kronik L, Loo YL, Lubomirsky I, Marder SR, Mastai Y, Miller JS, Mitzi DB, Paz Y, Rappe AM, Riess I, Rytchinski B, Stafsudd O, Stevanovic V, Toney MF, Zitoun D, Kahn A, Ginley D, Cahen D, Hybrid Organic-Inorganic Perovskites (HOIPs): Opportunities and Challenges, *Adv. Mater.*, 27(35), 5102-12 (2015).
- [5] Di Zhou, Tiantian Zhou, Yu Tian, Xiaolong Zhu, and Yafang Tu, Perovskite-Based Solar Cells: Materials, Methods, and Future Perspectives, *J. Nanomater.*, Volume 2018, Article ID 8148072, 15 pages.
- [6] Luis K Ono and Yabing Qi, Research progress on organic-inorganic halide perovskite materials and solar cells, *J. Phys. D: Appl. Phys.*, 51 (2018) 093001 (27pp).
- [7] Nitin Labhassetwar, Govindachetty Saravanan, Suresh Kumar Megarajan, Nilesh Manwar, Rohini Khobragade, Pradeep Doggali and Fabien Grasset, Perovskite-type catalytic materials for environmental applications, *Sci. Technol. Adv. Mater.*, 16 (2015) 036002.
- [8] Zhengqi Shi and Ahalapitiya H. Jayatissa, Perovskites-Based Solar Cells: A Review of Recent Progress, Materials and Processing Methods, *Materials (Basel)*, 11(5): 729 (2018).
- [9] M. Pazoki and T. Edvinsson, Metal replacement in perovskite solar cell materials: chemical bonding effects and optoelectronic properties, *Sustain. Energy Fuels*, 2, 1430 (2018).
- [10] Liang Chu, Waqar Ahmad, Wei Liu, Jian Yang, Rui Zhang, Yan Sun, Jianping Yang, Xing'ao Li, Lead-Free Halide Double Perovskite Materials: A New Superstar Toward Green and Stable Optoelectronic Applications, *Nano-Micro Lett.*, 11:16 (2019).
- [11] Rui Wang, M. Mujshif, Yu Duan, Zhao-Kui Wang, Jingjing Xue and Yang Yang, Review of Perovskites Solar Cell Stability, *Adv. Funct. Mater.*, 2019, 1808843.
- [12] Ajay Kumar Jena, Ashish Kulkarni, and Tsutomu Miyasaka, Halide Perovskite Photovoltaics: Background, Status, and Future Prospects, *Chem. Rev.*, 119, 3036 (2019).
- [13] Hilal Ahmad Reshi and Rayees Ahmad Zargar, Recent Development in Optoelectronic Devices, Chapter 7, *IntechOpen*, (2018).

- [14] Longbin Qiu, K. Ono and Yabing Qi, Advances and challenges to the commercialization of organic-inorganic halide perovskite solar cell technology, *Materials Today Energy*, 7, 169 (2008).
- [15] <https://www.advancedsciencenews.com/perovskite-perspectives-henry-snaith-and-zhiping>
- [16] <https://www.advancedsciencenews.com/perovskite-perspectives-weiguang-xie-and-jianbin>
- [17] <https://www.advancedsciencenews.com/perovskite-perspectives-jingbi-stoichiometry-bet>
- [18] <https://www.advancedsciencenews.com/perovskite-perspectives-yi-hou-christoph-brabec>
- [19] <https://www.advancedsciencenews.com/perovskite-perspectives-chul-ho-lee-min-jae-ko>

## Chapter 6

# HYBRID PEROVSKITES - SOLAR CELLS

The search for alternate energy conversion devices instead of using conventional fuels like fossil fuels, coal and other non-renewable sources has been more intense in the last decade and half. The extensive utilization of the inexhaustible source of sun's energy has been a dream source for many centuries though the extent of its utilization has always been small percentage. The anxiety has been increasing slowly, but from 2010 on wards, the concept of Solar Cells (devices which convert radiation into electricity directly) has assumed importance especially after the introduction of silicon based solar cells were introduced. Even though many varieties of solar cells have been proposed, cost and conversion efficiency are the factors that have been the main concern. The desire to compete with silicon based solar cells (nearly 26%) in terms of conversion efficiency, Perovskite based solar cells (with conversion efficiency already achieved around 22%) are proposed as alternate choice materials.

Perovskites, is named after the Russian mineralogist L. A. Perovski, with the general formula  $ABX_3$  (X = oxygen or halogen). The larger A cation occupies a cubo-octahedral site common with twelve X anions, the modest B cation is balanced out in an octahedral site with six X anions. The structure of a typical unit cell of perovskite is shown in Fig.1.

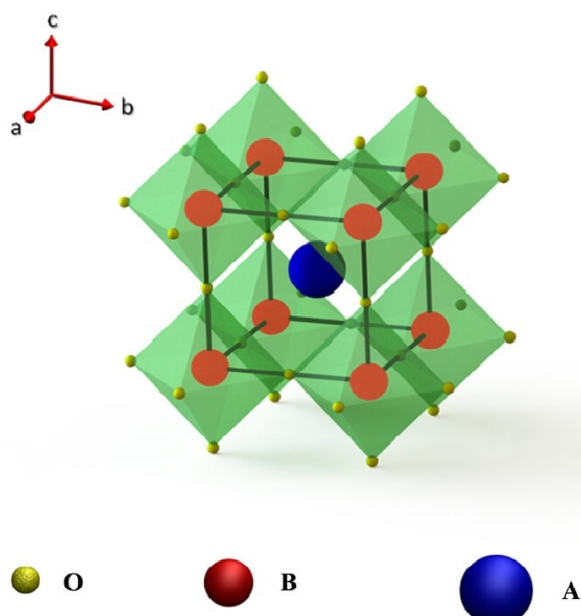


Figure 6.1: A typical Unit cell of Perovskite Structure

In general, photovoltaic performance of the perovskite solar cells is associated with their intrinsic properties like high absorption coefficient, tunable band gap, large carrier diffusion length, ambipolar carrier-transport ability and carrier mobility. The anxiety to make use of a variety of perovskites, a new concept was introduced namely hybrid perovskite (HOIP), where A cation is an organic moiety like methylammonium ( $\text{MA}^+$ ,  $\text{CH}_3\text{NH}_3^+$ ), formamidinium ( $\text{FA}^+$ ,  $\text{CH}_3\text{CH}_2\text{NH}_3^+$ ), while the B cation is the conventional inorganic cations like  $\text{Sn}^{2+}$ ,  $\text{Pb}^{4+}$  and X anions are usual halide ions. A simple pictorial representation of this hybrid system is shown in Fig.2.

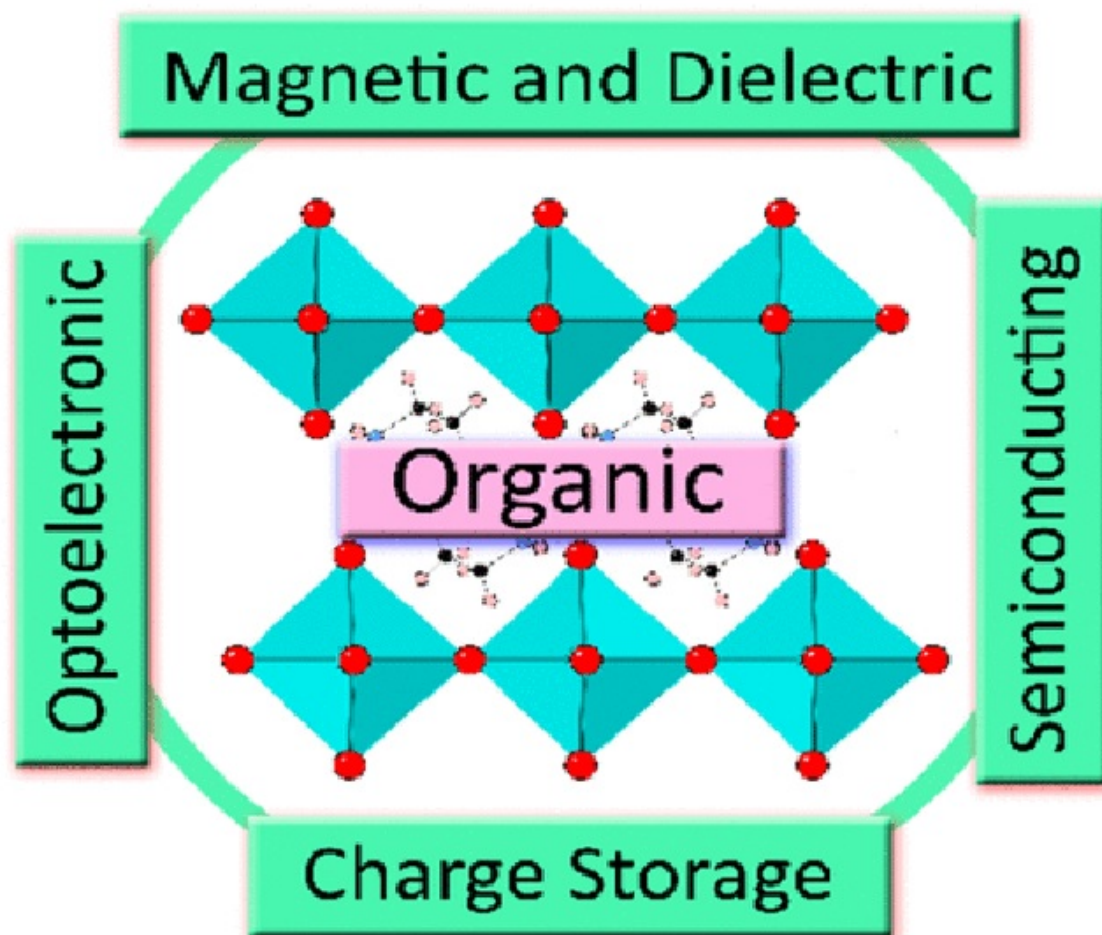


Figure 6.2: A pictorial representation of HOIP and their main properties and functions, The new properties result as a combination of two components

Further, in comparison to simple organic and inorganic semiconductors, the organic-inorganic hybrid perovskites exhibit unique optical and electrical properties. based on the concept of tolerance factor (see below) there have been attempts to predict various types of hybrid perovskites. One such attempt was made by Cheetham et al.[4] who have calculated the value of tolerance factor for over 2500 (for over 2500 prospective organic cation/metal halide-based anion  $\text{ABX}_3$ ) compounds and determined that over 700 have a consistent tolerance factor with the perovskite structure, with more than 600 of these being unknown hypothetical compounds as of 2015.. It is important to note that the concept of tolerance factor for ionic radii represents a necessary condition for the perovskite structure, and it has had significant success in predicting new perovskite structures; however, other space-filling considerations also need to be considered.

In addition, these OHIP materials consists of large Bohr radius, weak binding energy, high dielectric constant, high carrier diffusion velocity and diffusion length along with outstanding light absorbing capacity. Owing to all these advantages, the OHIP materials became the candidates for fabricating efficient solar cells with low cost. Normally, the perovskite solar cells consist an absorber layer (for example:  $\text{CH}_3\text{NH}_3\text{PbX}_3$ ), which is inserted between electron-transport layer (ETL) and hole-transport layer (HTL). When the perovskite-absorber is subjected to light it inserts an electron and hole into n-type and p-type carrier transporting materials in order to generate free charge carriers. The energy-levels and charge-transfer process the path for the charge carriers of perovskite solar cells are digramatically shown in Fig. 3. This means that the solar cells have to be made in a designed fashion with several layers stacked one above the other. This fabrication aspect will be taken up subsequently. Few words on the HTL and ETL will be in order at this stage.

## 6.1 Hole Transport Layer:

Electron-blocking materials are used as hole transportation materials in Perovskite Soolar cells (PSCs). The hole transport layer (HTL) assists in injecting the hole from the perovskite active layer and transfers the injected hole to the back electrode. The hole-transport layer also works as an electron-blocking layer that prevents electron flow The typical hole transport layers are, Spiro-OMeTAD (2,20,7,70-tetrakis-(N,N-di-p-methoxyphenylamine)-9,90-spiro-biurene), P3HT (Poly(3-hexylthiophene -2,5-diyl)), CuI-(Copper(I) iodide), CuSCN (Copper(I) thiocyanate), and so on.

## 6.2 Electron Transport Layer:

The layer that assists the injected electrons from the perovskite active layer to the front electrode is ETLs in the PSCs. The electron-transport layer also works as a hole-blocking layer that prevents the release of the holes to the front electrode, respectively. The typical electron transport layer is ZnO (Zinc Oxide),  $\text{TiO}_2$  (Titanium Dioxide),  $\text{SnO}_2$  (Tin (IV) oxide), IGZO (Indium-gallium-zinc oxide), PCBM (6,6-phenyl-C61-butyric acid methyl ester), and so on.

There are various aspects to be considered for the choice of ETL [Elelctron Transporting Layer ] and HTL [Hole Transporting Layer] materials for increasing the efficiency of solar cells. The materials must be defect free (to decrease or eliminate charge recombination centres), thin nature (to increase photon absorption and performance), adding dopants to increase carrier mobility (conductivity and charge transfer), altering the morphology,(surface roughness and grain size) multiple growth methods and these have also been suggested for improved performance of solar cells.

The selection of suitable electrode materials (anode and cathode) should be based on the energy positions so that the carrier transport is a facile process.This condition is shown pictorially in Fig.3.

When sunlight strikes a PSC [Perovskite Solar Cells], the perovskite material absorbes photon, excitons are formed, and charge transporters (electrons and holes) are formed upon exciton parting. Exciton parting occurs at the boundary between the charge-transporting layer and perovskite film. After the electron is detached from the hole and inserted into the Electron Transporting Layer (ETL), it travels to the anode usually made of fluorine doped tin oxide (FTO) glass. Instantaneously, the hole is inserted into the HTL and afferwards travels to the cathode (typically a metal).The holes and electrons are collected by counter and working

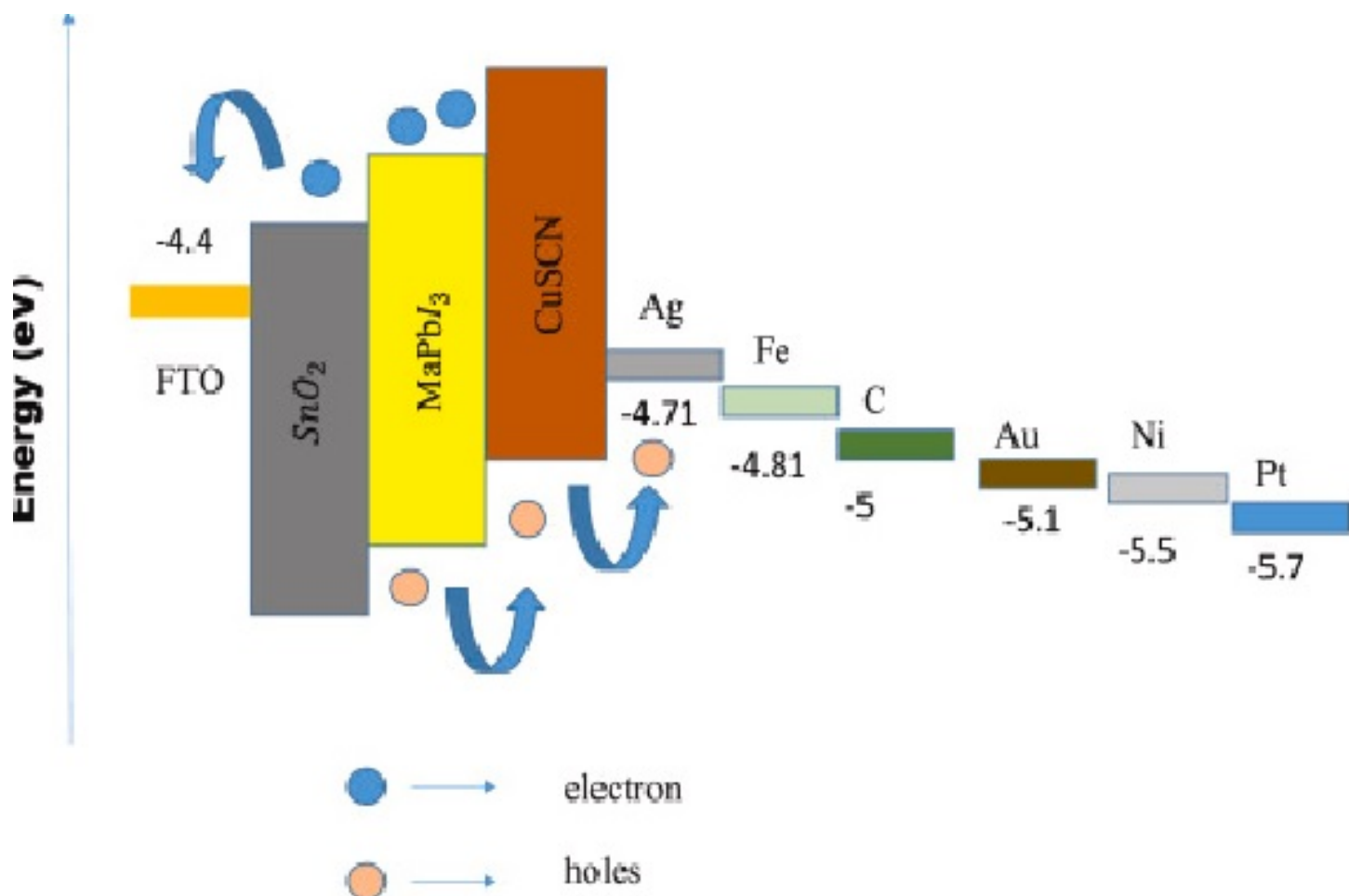


Figure 6.3: The different anodes and cathodes with their values of the work functions. Metals with different work function helps in tuning the magnitude and direction of electric field for better movement of light generated charge carriers.

electrodes, separately and moved to the outward circuit to generate current. This is the common general principle of typical solar cells. The steps involved can be listed as follows:

- Photon absorption trailed by the generation of free charge
- Transport of charge
- Extraction of charge

The structure adopted by ions and species depends on their radii and rigidity. Two critical factors for crystallizing in a perovskite structure are the octahedral factor (coordination factor) and the tolerance factor. The tolerance factor, defined as the ratio of bond lengths A–X to B–X in a perfect solid-sphere model, is scientifically expressed as:

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

where  $R_A$ ,  $R_B$ , and  $R_X$  are the ionic radii of corresponding ions. The tolerance factor  $t$  must satisfy  $0.8 \leq t \leq 1.0$  for 3D perovskites. This concept has been discussed in earlier chapters. Lower values of  $t$  result in less symmetric tetragonal or orthorhombic structures, while values of  $t$  greater than 1 could destabilize the 3D B–X system.

For simple elemental inorganic ions, assigning an ionic radius is straightforward. However, molecular ions used in HIOPs (Hybrid Inorganic-Organic Perovskites) pose limitations due to



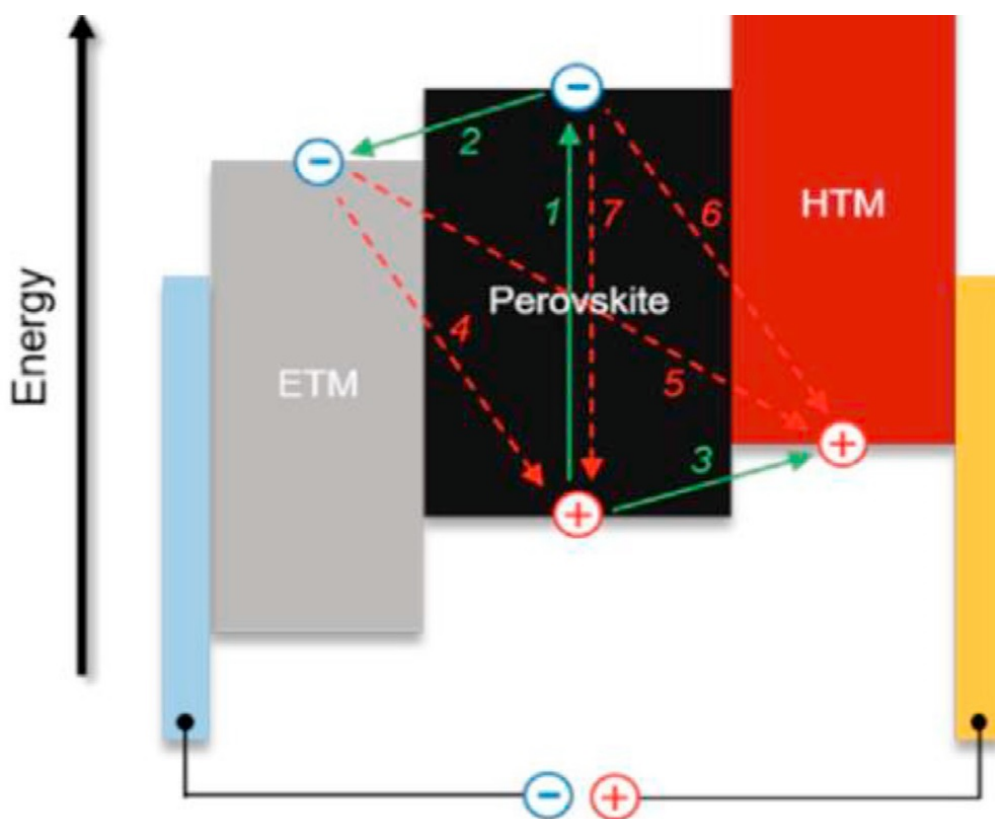


Figure 6.4: The electron and hole paths. Reproduced from Ameen S, Akhtar MS, Shin H-S, Nazeeruddin MK. Charge-transporting materials for perovskite solar cells. *Adv Inorg Chem* 2018:185e246. doi.org/10.1016/bs.adioch.2018.05.009

potential free rotation around their center of mass. Ionic radii of some organic cations found at the A site are listed in Table 1, based on values reported by Kieslich et al. [4] or Becher et al. [19].

In Table 1, the values that are normally associated with these type of ions are assembled. The choice of the two cations A and B depends on the anion and if the anion is a halide ion A must be univalent cation and B can be a divalent cation. In general, it must be ensured that the total cationic charge can compensate for the total anionic charge. For example two B cations with charge +1 and +3 can be equally substituted in the B site so that the net cationic charge can be +2. This only shows that a variety of perovskites can be generated by suitable substitution at both A and B sites and hence a variety perovskite materials can be generated.

In addition to size and charge, there are also the bonding/coordination preferences for the metal ions involved. The dimensionality from 3D to lower order (2D or less) the restrictions imposed by the value of tolerance factor is relaxed and For example, in two-dimensional (2-D) layered derivatives of the perovskite structure, there are no known restrictions for the interlayer “A” cation length and, in the 0-D derivatives, size restrictions are not applicable altogether, as  $\text{MX}_6$  octahedra are isolated and can readily shift in relative position. This structural flexibility and tunability of the dimensionality provide a rich and fertile “playground” for the preparation of interesting crystal structures with varying physical properties and also structural variations. Even though, it is considered that size restrictions may be relaxed for the lower dimensional perovskites, there are still other important parameters to be considered for the successful design and synthesis of a desired perovskite-related structure. The organic cation “A” must contain terminal functional groups that can ionically interact with the anionic inorganic substructure,

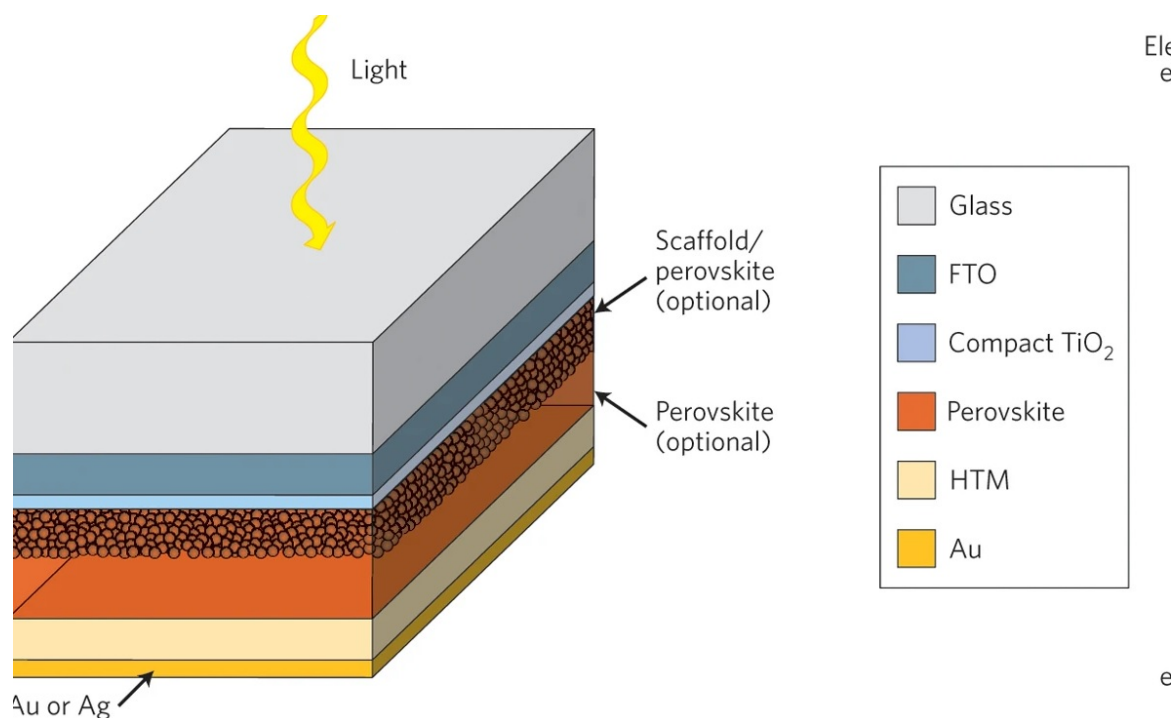


Figure 6.5: A diagrammatic design of solar cell

but without the rest of the organic molecule interfering with the inorganic components “B” and “X”. Most of the known layered perovskite derivatives feature mono- or diammonium cations, yielding the general formulas of  $(\text{RNH}_3)_2\text{BX}_4$ , where “R” represents an organic functional group. The presence of ammonium cations leads to various hydrogen bonding schemes with the anionic substructure, which are important for determining the orientation and conformation of the interlayer organic cations. Depending on the choice of metal, the inorganic framework can be more or less rigid, which also influences the hydrogen bonding schemes.

In general, both the organic cations and the anionic inorganic framework have templating influence on each other on the basis of size, width and length, allowing a certain degree of control over the final structures adopted and the resultant properties.

### 6.3 Opto-Electronic Property

Even though, initially it was considered that the organic moiety in HOIPs is only fulfilling the space filling function, the organic moiety now is known to alter the HOMO-LUMO energy levels and thereby enabling an active role in the opto-electronic properties of the solid.

The Perovskite Solar cells (PSCs) quick increase in PCE from 3.8% to nearly 25.2% within a decade (as shown in the previous sections) indicates their potential for exploitation. The approach to efficiency increase included changes to the device architecture, (various architectures like Mesoporous perovskite solar cell, Regular planar perovskite solar cell, Inverted planar perovskite solar cell, and so on), new carrier transport materials (ETLs and HTLs), and improvements to the absorber layer. The alteration of the anionic and cationic components, such as the use of FA along with MA and mixed halides, improves the absorber layer. The structural and opto-electronic characteristics of the film depend on the added solvent, the method used to make the film, the annealing temperature, and environmental factors like temperature, moisture content, oxygen, and others in addition to the organic and inorganic components in the perovskite layer. To design an effective PSC, it is necessary to have a control over the stoichiometry, grain structure, and crystallographic phase of the perovskite layer.

Table 6.1: Typical values of ionic radii for some cations and anions commonly found in perovskite lattices. The two values given for some cations refer to those reported by Kieslich et al. [4] and Becker et al. [19].

Anion	Effective radius $r_{X,\text{eff}}$ (pm)
Fluoride	129
Chloride	181
Bromide	196
Iodide $\text{I}^-$	220
Formate $\text{HCOO}^-$	136
Oxide $\text{O}^{2-}$	146
Sulfide $\text{S}^{2-}$	184
Selenide $\text{Se}^{2-}$	192
Cyanide $(\text{CN})^-$	...
Nitride ( $\text{N}_3$ )	140 (approx.)
Borohydride $(\text{BH}_4^-)$	...

## 6.4 Factors Influencing the Performance of Perovskite Materials

Let us consider briefly the various factors that influence the performance of perovskite materials.

### 6.4.1 Solar Radiation

It is known that seasonal variations can cause the extent of solar energy in the range  $1.4 \text{ kW/m}^2$  to  $1.31 \text{ kW/m}^2$ . at the earth means distance from the sun. The wavelength range of 250 nm - 3000 nm accounts for more than 80% of solar electricity. Photons with a wavelength approaching 600 nm have the highest intensity in this solar spectrum. In addition, the effect of turbidity, ground reaction, and scattering are not negligible but they are not considered usually. A certain solar spectrum undergoing specific conditions is leveled with an air mass (**AM**) standard symbol. Some of the scales normally used to denote the solar radiation are defined as follows: **AM0** denotes the sun spectrum outside of the atmosphere. At that point, the actual path length of solar radiation is assumed to be zero. **AM1**: The equator and its environs receive sun radiation with a zenith angle of 00, resulting in an AM coefficient of 1. **AM1.5** It is the conventional solar spectrum, with  $\theta = 48.20^\circ$ , that's used in solar cell testing on the ground. The majority of the world's population lives in a moderate climate zone between the tropics and the arctic.

### 6.4.2 Influence of Thickness

One of the important approaches for The  $\text{MAPbI}_3$  based PSC device is accomplished using this parameter. It is known that the short circuit current increases as the material exposed to light increases and thus gives rise higher excitons generation. But still higher thickness, a recombination effect comes to play in the PSC device. .

Table 6.2: Typical values of effective ionic radii for some cations commonly found in perovskite lattices. The two values given for some cations refer to those reported by Kieslich et al. [4] and Becker et al. [19].

Cation	Effective radius $r_{A,\text{eff}}$ (pm)
Ammonium $[\text{NH}_4]^+$	146, 170
Hydroxylammonium $[\text{H}_3\text{NOH}]^+$	216, 226
Methylammonium $[\text{CH}_3\text{NH}_3]^+$	217, 238
Hydrazinium $[\text{H}_3\text{N-NH}_2]^+$	217
Azetidinium $[(\text{CH}_2)_3\text{NH}_2]^+$	250, 284
Formamidinium $[\text{NH}_2(\text{CH})\text{NH}_2]^+$	253, 277
Imidazolium $[\text{C}_3\text{N}_2\text{H}_5]^+$	258, 303
Dimethylammonium $[(\text{CH}_3)_2\text{NH}_2]^+$	272, 296
3-Pyrrolinium $[\text{NC}_4\text{H}_8]^+$	272
Thiazolium $[\text{C}_3\text{H}_4\text{NS}]^+$	320
Ethylammonium $[\text{C}_2\text{H}_5\text{NH}_3]^+$	274
Guanidinium $[\text{C}(\text{NH}_2)_3]^+$	278, 280
Tetramethylammonium $[(\text{CH}_3)_4\text{N}]^+$	292, 301
Piperazinium $[\text{C}_4\text{H}_{12}\text{N}_2]^{2+}$	322
Tropylium $[\text{C}_7\text{H}_7]^+$	333
Dabconium $[\text{C}_6\text{H}_{14}\text{N}_2]^{2+}$	339
$[\text{C}_7\text{H}_7]^+$	...
$[(\text{CH}_2)_4\text{NH}_2]^+$	...
$[(\text{HN})(\text{CH}_2)_3\text{S}]$	...
$[(\text{CH}_3)(\text{NH}_3)]^+$	317, 238

### 6.4.3 Influence of Defect Density

Another parameter that influences the overall outputs of the perovskite devices is the defect density. The bulk defect density significantly impacts the performance of perovskite solar cells. Incomplete dangling bonds within the material leads to additional trap energy levels within the band gap and these levels act as a recombination centre and reduce the carrier lifetime. These defect levels can be passivated by using compositional, chemical, or material engineering to reduce the defect density and increase the carrier lifetime for better performance. The defect density is known to affect both the short circuit current and also open circuit voltage.

### 6.4.4 Influence of Temperature

Thermal instability is a concern for researchers and scientists in Perovskite Solar cells (PSCs). The fact that annealing is a critical stage in the fabrication of perovskite films indicates that perovskites will likely be exposed to high temperatures. The operating temperature for solar cells ranges from 300 K to 400 K; hence, the newly fabricated perovskite solar cells must be able to tolerate high temperature conditions. Research has shown that the  $\text{MAPbI}_3$  active layer has a very low thermal conductivity and also degrades at a temperature of 85 °C even in an inert atmosphere. On the contrary, the constituent material in the perovskite structure, in the  $\text{ABX}_3$  type of structure, where A is a cation and primarily an organic cation component, is a volatile substance in nature that tends to degrade at high temperatures.

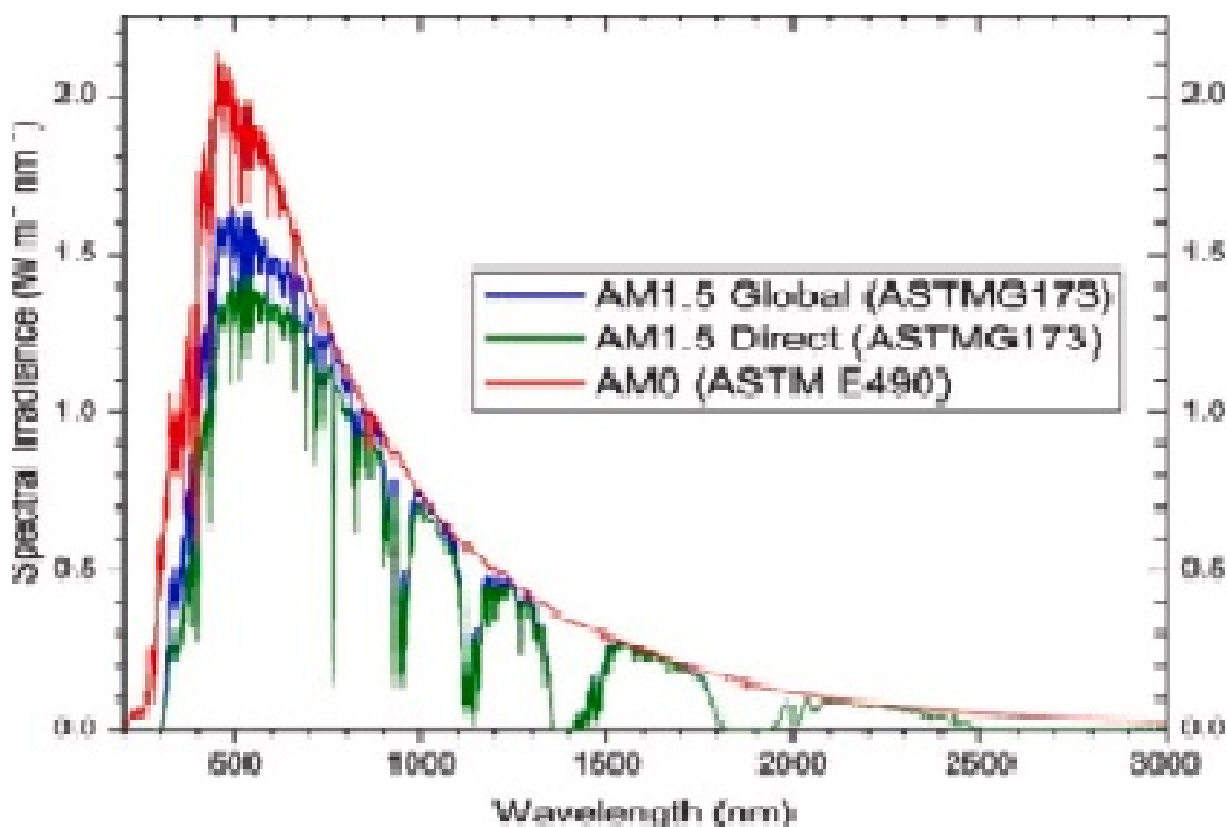


Figure 6.6: Comparison between the AM0, AM1, and AM1.5 solar spectrum.

#### 6.4.5 Influence of Moisture Content and Oxygen

The problem PSCs encounter is the perovskite layer's interaction with oxygen and water molecules. This is an inevitable occurrence that happens even when cells are being tested and put together. When water molecules react with the  $ABX_3$  layer, the layer separates into its component parts. Taking  $MAPbI_3$  layer as a standard example, the breakdown route is explored. It first degrades into the original MAI and  $PbI_2$ , then creates aqueous HI, solid  $PbI_2$ , and volatile  $CH_3NH_2$  as a result. The hygroscopic nature of the amine salts generally causes the instability caused by moisture. In the presence of moisture, the behavior of  $MAPbI_{3-x}Cl_x$  and  $MAPbI_3$  is similar: MA sublimates, leaving just  $PbI_2$  remaining. The substance is hydrophilic, which causes it to rapidly absorb water from its environment and result in the fabrication of compounds that resemble hydrates ( $CH_3NH_3$ ) $4PbI_6 \cdot 2H_2O$ )

#### 6.4.6 Influence of Other Effects

Due to the ionic conductivity and low Frenkel and Schottky defect generation energies, the behavior of PSCs under electrical bias is a cause for concern. According to several theoretical research, the vacancy enhanced  $FA^+$ ,  $MA^+$ , and ion movement. The ions low activation energies, which range from 0.1 to 0.8 eV, are equivalent to the energies of the ions in conduc-

tors. These ions can readily aggregate and migrate at the perovskite/contact interface under biased conditions, which lowers the internal potential and charge collection efficiency. The hybrid organic-inorganic perovskites have ionic characteristics and low ion migration activation energy.

## 6.5 The Challenges

The performance of the device, cost, and stability are the three determining elements for a solar cell's commercial viability. At this time, maintaining long-term stability at the module level and ensuring reliable outdoor operation are the biggest difficulties facing PSCs. There must be standards for the stability measuring methodologies. one has to have a stadard method to accurately anticipate the lifespan of PSCs under operating settings. The performance decay brought on by illumination and heat should be addressed.

The lifespan and efficiency of solar panels significantly impact cost per kilowatt-hour. The availability of abundance and cheap raw materials of PSC processing leads to cutting manufacturing costs below those of traditional PV systems. Indeed, PSCs become commercially competitive due to the lower production cost, which can eventually decrease the cost of the whole module.

# Bibliography

- [1] N. Suresh Kumar a, K. Chandra Babu Naidu, A review on perovskite solar cells (PSCs), materials and applications, *Journal of Materiomics* textbf7, (2021), 940-956.
- [2] Rabia Sharif, Arshi Khalid, Syed Waqas Ahmad, Abdul Rehman, Haji Ghulam Qutab, Hafiz Husnain Akhtar, Khalid Mahmood, Shabana Afzal and Faisal Saleem, A comprehensive review of the current progresses and material advances in perovskite solar cells, *Nanoscale Adv.*, (2023), **5**,3803.
- [3] B.Viswanathan, V. Suryakumar, B. Venugopal, SH Rosjima amd N.Hariprasad, Perovskite Materials an Introduction, e-book from National Centre for Catalysis Research, IIT, Madras (2019).
- [4] Kieslich, G.; Sun, S.; Cheetham, A. K. An Extended Tolerance Factor Approach for Organic-Inorganic Perovskites *Chem. Sci.* (2015), **6**, 3430– 3433 DOI: 10.1039/C5SC00961H; G. Kieslich , S. Sun and A. K. Cheetham , *Chem. Sci.*, 2014, **5** , 4712 —4715.
- [5] Jeon NJ, Noh JH, Kim YC, Yang WS, Ryu S, Seok SI.Solvent engineering for high-performance inorganic–organic hybrid perovskite solar cells, *Nat Mater* (2014);**13**:897.
- [6] Liu D, Kelly TL.Perovskite solar cells with a planar heterojunction structure prepared using room-temperature solution processing techniques, *Nat Photonics*, (2013),**8**,133.
- [7] Hong F, Saparov B, Meng W, Xiao Z, Mitzi DB, Yan Y.Viability of Lead-Free Perovskites with Mixed Chalcogen and Halogen Anions for Photovoltaic Applications, *J Phys Chem C* (2016),**120**6435.
- [8] Saparov B, Sun J-P, Meng W, Xiao Z, Duan H-S, Gunawan O, Shin D, Hill IG, Yan Y, Mitzi, Thin-Film Deposition and Characterization of a Sn-Deficient Perovskite Derivative  $\text{Cs}_2\text{SnI}_6$ , *Chem Mater* (2016)**28**,2315.
- [9] Xiao Z, Meng W, Wang J, Mitzi DB, Yan Y.Searching for promising new perovskite-based photovoltaic absorbers: the importance of electronic dimensionality, *Mater Horiz*, (2017) **4**,206.
- [10] Xiao, Z.; Meng, W.; Saparov, B.; Duan, H.-S.; Wang, C.; Feng,C.; Liao, W.; Ke, W.; Zhao, D.; Wang, J.; Mitzi, D. B.; Yan, Y.Photovoltaic Properties of Two-Dimensional  $(\text{CH}_3 \text{NH}_3)_2 \text{Pb}(\text{SCN})_3 \text{I}_2$  Perovskite: A Combined Experimental and Density Functional Theory Study., *J. Phys. Chem. Lett.* (2016),**7**, 1213-1218.
- [11] Yu Y, Wang C, Grice CR, Shrestha N, Zhao D, Liao W, Guan L, Awni RA,Meng W, Cimaroli AJ, Zhu K, Ellingson RJ, Yan Y. Synergistic Effects of Lead Thiocyanate Additive and Solvent Annealing on the Performance of Wide-Bandgap Perovskite Solar Cells *ACS Energy Lett* (2017);**2**,1177.

- [12] Liao W, Zhao D, Yu Y, Grice CR, Wang C, Cimaroli AJ, Schulz P, Meng W, Zhu K, Xiong RG, Yan Y. Lead-Free Inverted Planar Formamidinium Tin Triiodide Perovskite Solar Cells Achieving Power Conversion Efficiencies up to 6.22%, *Adv Mater*, (2016), **28**,9333.
- [13] Mitzi, D. B. Synthesis, Structure and Properties of Organic-Inorganic Perovskites and Related Materials Prog. Inorg. Chem. 1999, 48, 1– 121 DOI: 10.1002/9780470166499.
- [14] Mitzi, D. B. Templating and Structural Engineering in Organic-Inorganic Perovskites J. Chem. Soc., Dalton Trans. 2001, 1– 12 DOI: 10.1039/b007070j
- [15] Goldschmidt, V. M. Die Gesetze der Krystallochemie *Naturwissenschaften* 1926, 14, 477–485 DOI: 10.1007/BF01507527.
- [16] Rabia Sharif, Arshi Khalid, Syed Waqas Ahmad, Abdul Rehman, Haji Ghulam Qutab, Hafiz Husnain Akhtar, Khalid Mahmood, Shabana Afzal and Faisal Saleem. A comprehensive review of the current progresses and material advances in perovskite solar cells, *Nanoscale Adv.*, (2023), **5**,3803.
- [17] Bayrammurad Saparov and David B. Mitzi, Organic–Inorganic Perovskites: Structural Versatility for Functional Materials Design, *Chem. Rev.*, (2016),**116**, 7, 4558–4596.
- [18] M. A. Green, A. Ho-Baillie and H. J. Snaith, The emergence of perovskite solar cells, *Nat. Photonics*, (2014), **8(7)**, 506–514.
- [19] M. Becker , T. Klüner and M. Wark ,Formation of hybrid ABX<sub>3</sub> perovskite compounds for solar cell application: first-principles calculations of effective ionic radii and determination of tolerance factors† *Dalton Trans.*, (2017), **46** , 3500.
- [20] Sagar Bhattarai, Asya Mhamdi, Ismail Hossain, Yassine Raoui, Rahul Pandey, Jaya Madan, Abdelaziz Bouazizi, Madhusudan Maiti, Dipankar Gogoi, Arvind Sharma, A detailed review of perovskite solar cells: Introduction, working principle, modelling, fabrication techniques, future challenges, *Micro and Nanostructures*, **172**(2022), 207450



# INDEX

Goldschmidt's Tolerance Factor  
Opto Electronic Property  
Hole transporting layer (HTL)  
Electron transporting Layer (ETL)  
Perovskite solar cell (PSC)  
A site cation  
B site cation  
X anion