PEROVSKITE MATERIALS- AN INTRODUCTION

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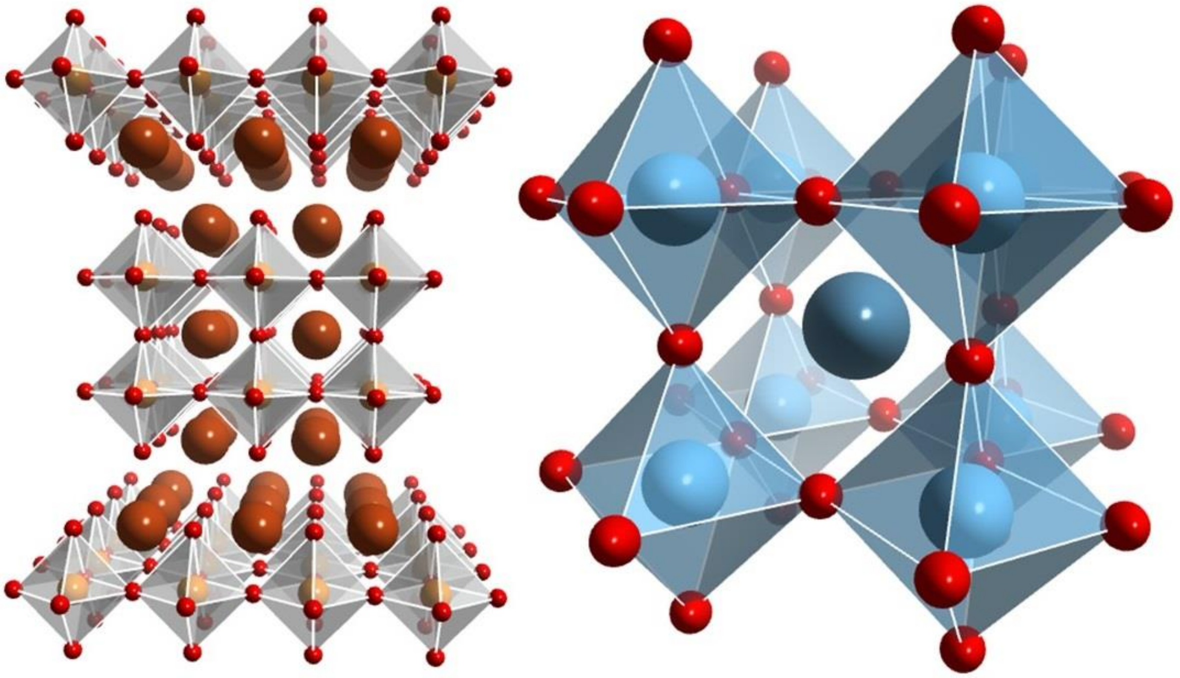

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Perovskites: An Introduction

53 pages and 27 figures

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PREFACE

National Centre for Catalysis Research (NCCR) at the Indian Institute of Technology, Madras has been generating some of the e-books specifically meant for educational and knowledge assimilation purpose. In this direction, it was considered that a concise and straightforward textbook on perovskite materials (the material that has received considerable attention of the scientific world in recent times mainly from the point of view of device applications) would be useful for the younger generation so that they can make more innovative applications of this beautiful solid state material.

It has been realised that the vast amount of information available on this solid-state material cannot be contained in a single textbook, and hence this compilation cannot be considered to be comprehensive on this subject. In order to keep the subject matter simple, it is attempted in this compilation to deal with certain specific aspects like the structural aspects of these materials and the factors controlling the crystallization in perovskite structure and also to give a flavor of the recent developments in this field a chapter on Hybrid Organic-Inorganic Perovskites (HOIPs) has been included in this short monograph.

The motivation and enthusiasm shown by the members of NCCR (especially Mr. Surya Kumar, Mr. Hariprasad Narayanan, Roshna and all other research scholars of NCCR and elsewhere) in attempting this compilation deserve special mention, and we are grateful to them. As stated above, this compilation is only meant as a learning resource, and hence it is kept to the minimum size and the contents have been chosen so that even a high school student can follow and use it as a knowledge source.

The members of NCCR are aware of the limitations and shortcomings involved in such an endeavour. We will be ever grateful to any of the suggestions to improve our efforts. The feedback in any form will be the cornerstone for our future such efforts.

Dated 30Th June 2019

Place: Chennai 600 036 **B. Viswanathan**

Contents

CHAPTER 1

INTRODUCTION

Material Science – the Emerging Discipline

In this century, Material Science will dominate the research and application fields due to various reasons, mainly because of their application 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 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 initiate 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 lifestyle in terms of time and comfort. Metal oxides represent 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 1.1. Many of these systems are naturally found. Their properties can be effectively utilised in some of the solid-state devices now in use [2].

Table 1.1. Some of the Known Oxide Materials

Name of the structures	Typical examples	Typical uses
Perovskite	$CaTiO_3$	Solar cells, opto electronics
Spinel	$MgAl_2O_4$, Fe_3O_4	Ferrimagnetism
Olivine	Mg_2SiO_4, Fe_2SiO_4	Gemstone
Ilmenite	$FeTiO_3$	Ore for Ti
Fluorite	CaF_2	Fluorescence
Pyrochlore	$(Na,Ca)_2Nb_2O_6F$	Magnetic property
Garnet	$X_3Y_2(SiO_4)_3$	Magnetic Property
Rutile	TiO_2	Semiconductor, Photocatalyst

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, $MgTiO_3$) 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 it. At high pressures, the silicate mineral olivine transforms into ringwoodite spinal structure, and very high pressure transforms it to perovskite structure [3].

$$Mg_2SiO_4 \text{ (Olivine)} \rightarrow SiMg_2O_4 \text{ (Spinel)} \rightarrow MgSiO_3 \text{ (Perovskite)} + MgO \text{ (Periclase)}$$

Table 1.2. Phase transformations in the earth mantle. Reproduced from [3]

Depth (km)	Phase Transformation
Transition Zone	
410	Olivine (α-(Mg, Fe)$_2$SiO$_4$) $\leftrightharpoons$ Wadsleyite (β-(Mg, Fe)$_2$SiO$_4$)
450	Kyanite (Al_2SiO_5) $\leftrightharpoons$ Corundum (Al_2O_3) + Stishovite (SiO_2(tetr.))
520	Wadsleyite (β-(Mg, Fe)$_2$SiO$_4$) $\leftrightharpoons$ Ringwoodite (γ-(Mg, Fe)$_2$SiO$_4$)
400-600	Pyroxene ((Mg,Fe)$_2$Si$_2$O$_6$)$\leftrightharpoons$ Majorite (Mg$_3$(MgSi)Si$_3$O$_{12}$)
Lower Mantle	
670	Ringwoodite (γ-(Mg, Fe)$_2$SiO$_4$) $\leftrightharpoons$ Perovskite ((Mg, Fe) SiO$_3$) + magnesio-wustite (Fe, Mg) O
850-900	Pyrope ($Mg_3Al_2Si_3O_{12}$) $\leftrightharpoons$ Perovskite ((Mg, Fe) SiO$_3$) + Sodium solution of Corundum (Al_2O_3) and ilmenite ((Mg, Fe) SiO$_3$)
1200	Stishovite (SiO_2) $\leftrightharpoons$ SiO_2 ($CaCl_2$ sturcture)
1700	Metalisation of chemical bonds in Wustite (FeO)
2000	SiO_2 ($CaCl_2$ sturcture) $\leftrightharpoons$ SiO_2 (structure intermediate between PbO and ZrO_2)
2200-2300	Corundum (Al_2O_3) $\leftrightharpoons$ Al_2O_3 (Rh_2O_3 structure)
D" layer	
2800-2900	Complicated phase relations, partial melt
Outer Core	
2900	Liquid Iron

Perovskite means calcium titanate ($CaTiO_3$), 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, come 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].

Table 1.3. Genesis and evolution perovskite structure and its applications. Reproduced from [6]

Period	**Inventors/Organization**	**Description**
1839	Gustav Rose (Berlin, Germany)	During an expedition in Russia, he discovered the mineral based on CaTiO3 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 MgSiO3 perovskite.
1964	Compagni e 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 a 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.
1988	Sharp (Osaka, Japan)	Developed a thermoelectric material with a perovskite structure composed of a rare earth element and a transition metal.
1994	D.B. Mitzi et al./ IBM (Yorktown Heights, N.Y.)	Developed luminescent organic-inorganic halide perovskites for light-emitting devices.
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 & 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 the first devices, and the first

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.

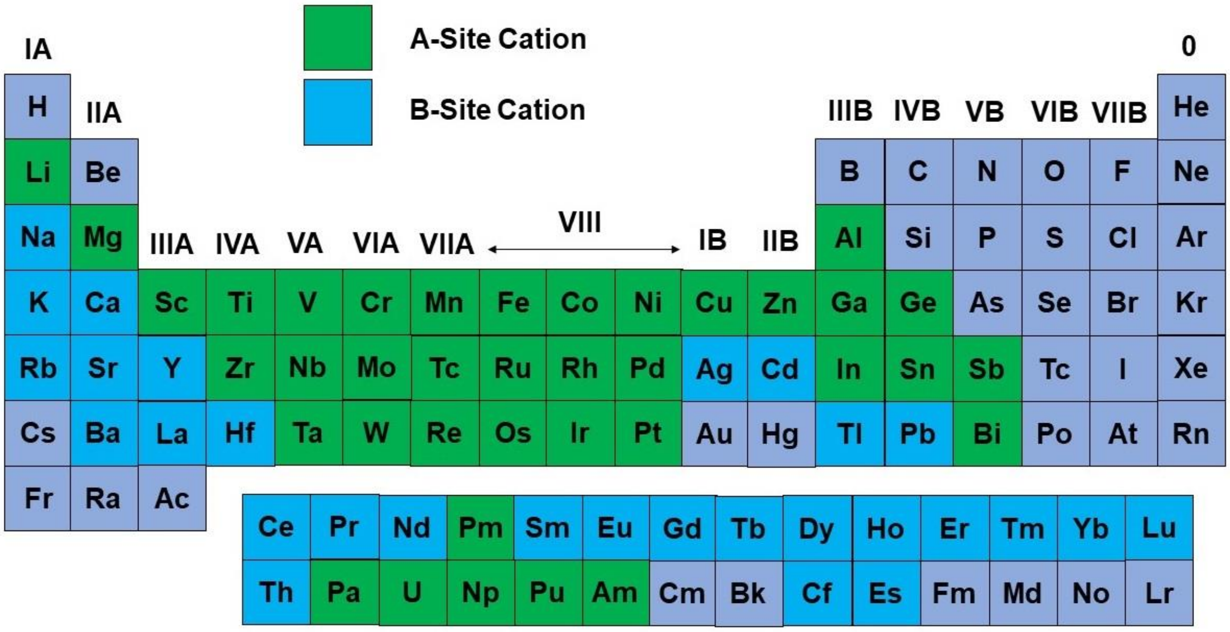

Fig.1.1. Periodic table showing the elements that occupy A or B site cationic positions in the perovskite structure.

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

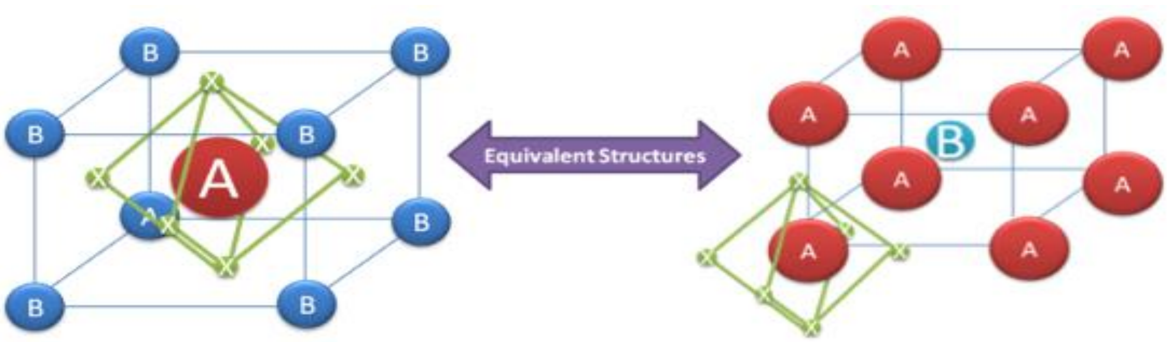

Fig.1.2. Two equivalent structures of perovskite structures with left-hand side is drawn with B site ion at <0,0,0> and the right-hand diagram with A site ions at <0,0,0> position [10].

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: ABO_3-perovskite (ex: $BaTiO_3$, $CaTiO_3$), A_2BO_4-Layered perovskite (ex: Sr_2RuO_4, K_2NiF_4), A_2 BB'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 studies 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 been 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].

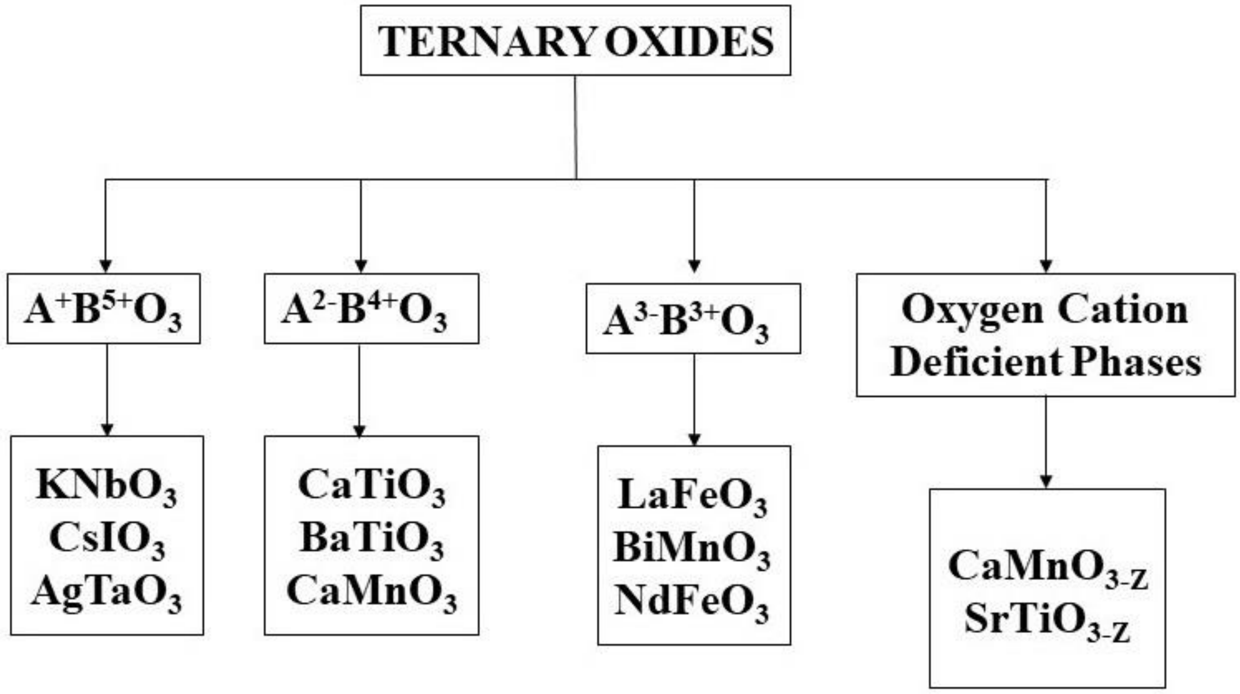

Fig.1.3. Flow diagram of the generation of a variety of compositions in ABX_3 systems [11].

Properties of Perovskites

Perovskite is a new derivative of a close-packed structure in which the oxygen arranged in a cubic close-packed arrangement except one oxygen 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, orthorhombic 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 superconductor shows resemblance with perovskite structure. In these superconducting structures, Cu substitutes the Ti in the layers and show unusual superconductivity at elevated temperature.

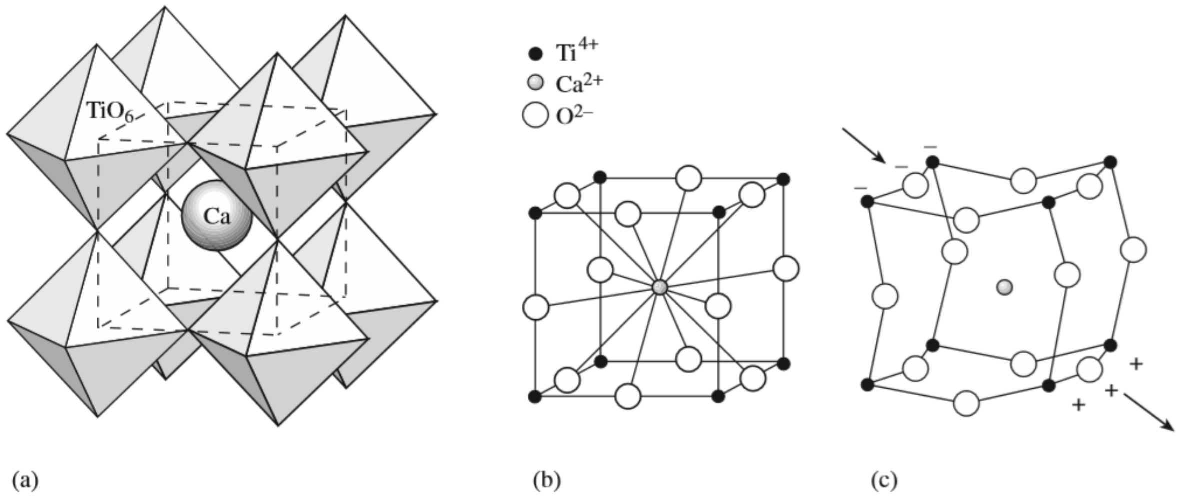

Figure 1.4. (a) Polyhedral representation of the structure of perovskite, showing the large 12-fold coordinated Ca^{2+} in the centre of the cubic unit cell and the smaller 8-fold coordinated Ti^{4+} in the corners. (b) Representation of perovskite structure with small spheres. (c) The perovskite structure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

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 thus find many practical applications. These solids are currently gaining considerable importance in the field of electronics, geophysics, astrophysics, nuclear, optics, medical, environment, optoelectronics, 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, catalyst behaviour and solar energy conversion. Depending on these distinct properties perovskite 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 & underwater devices, (16) microwave devises and so on. Perovskites exhibit many new and unique properties, and some of the properties exhibited by typical perovskites are assembled in Table 1.4.

Table 1.4. Some of the Properties Exhibited by Typical Perovskite Oxides

Compound	**Properties**	**Applications**	**Notes**
$BaTiO_3$	Ferroelectricity, piezoelectricity, high dielectric constant	Multilayer ceramic capacitors (MLCCs), PTCR resistors, embedded capacitance	Most widely used dielectric ceramic TC = 125°C
(Ba, Sr) TiO_3	Non-linear dielectric properties	Tunable microwave devices	Used in the paraelectric state
(Pb, Zr) TiO_3	Ferroelectricity, piezoelectricity	Piezoelectric transducers and actuators, ferroelectric memories (FERAMs)	PZT: most successful piezoelectric material
$Bi_4Ti_3O_{12}$	Ferroelectric with high Curie Temperature (T_C)	High-temperature actuators, FeRAMs	Aurivillius compound T_C = 675°C
$(K_{0.5}Na_{0.5})$ NbO_3, $Na_{0.5}Bi_{0.5}TiO_3$	Ferroelectricity, piezoelectricity	Lead-free piezoceramics	Performances not yet comparable to PZT but rapid progress
$(Pb,La)(Ti,Zr)O_3$	Transparent ferroelectric	Optoelectronic devices	First transparent ferroelectric ceramic
$BiFeO_3$	Magnetoelectric coupling, high Curie temperature	Magnetic field detectors, memories	Most investigated multiferroic compound. T_C = 850°C

$PbMg_{1/3}Nb_{2/3}O_3$	Relaxor ferroelectric	Capacitors, actuators	High permittivity, significant electrostrictive coefficients, frequency-dependent properties
$SrRuO_3$	Ferromagnetism	Electrode material for epitaxial ferroelectric thin films	
(La, A) MnO_3 A = Ca, Sr, Ba	Ferromagnetism, giant magnetoresistance, spinpolarized electrons	Magnetic field sensors, spin electronic devices	
$SrTiO_3$	Incipient ferroelectricity, thermoelectric power, metallic electronic conduction when n-doped, mixed conduction when p-doped, photocatalyst	Alternative gate dielectric material, barrier layer capacitors, a substrate for epitaxial growth, photo-assisted water splitting	Multifunctional material
$LaGaO_3$ $BaIn_2O_5$	Oxide-ion conduction	The electrolyte in solid oxide fuel cells (SOFCs)	$BaIn_2O_5$ is an oxygen-deficient perovskite with brownmillerite structure.
$BaCeO_3$, $BaZrO_3$	Proton conduction	The electrolyte in protonic solid oxide fuel cells (PSOFCs)	High protic conduction at 500-700°
(La, Sr) BO_3 B=Mn, Fe, Co	Mixed conduction, catalyst	The cathode material in SOFCs, oxygen separation membranes, membrane reactors, controlled oxidation of hydrocarbons.	Used for SOFC cathodes
$LaAlO_3$ $YAlO_3$	Host materials for rare-earth luminescent ions	Lasers Substrates for epitaxial film deposition	

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 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 realised through 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. This aspect will be considered subsequently.

The crystallisation in perovskite structure is considered in terms of tolerance factor defined (discussed in a subsequent chapter) in terms of cation and anion radii, and the universal applicability of this concept for adopting perovskite structure needs a careful examination. Though this aspect has not been adequately treated in this presentation, it deserves careful examination.

There are a variety of questions that one can have on perovskites 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.

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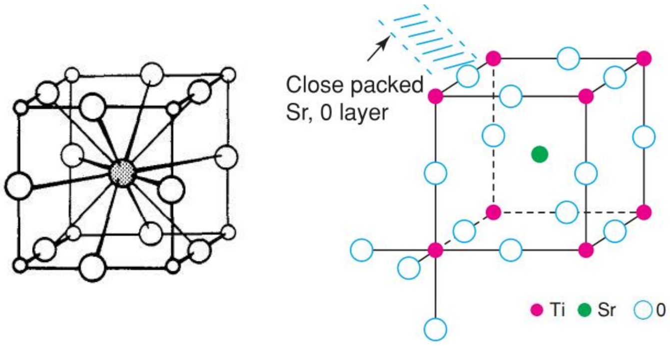
CHAPTER 2

STRUCTURE OF PEROVSKITES

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.



a b

Figure 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 views for better visualisation.

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 & 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).

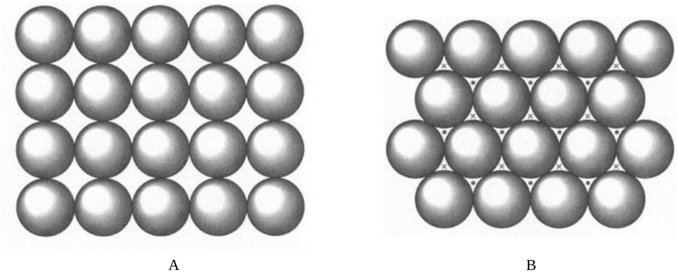


Figure 2. (a) A square array of spheres; (b) a close-packed layer of spheres.[3]

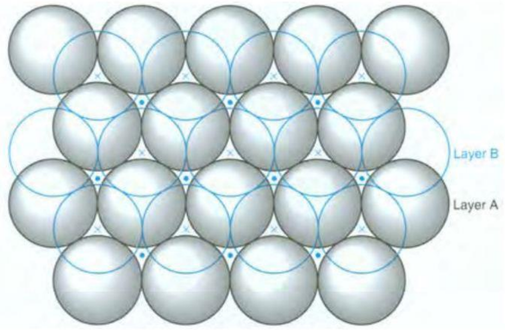


Figure 3. Two layers of close-packed spheres.[3]

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 cp structure, each sphere is in contact with with12 others, and this is the maximum coordination number possible for contacting and equal-sized spheres.

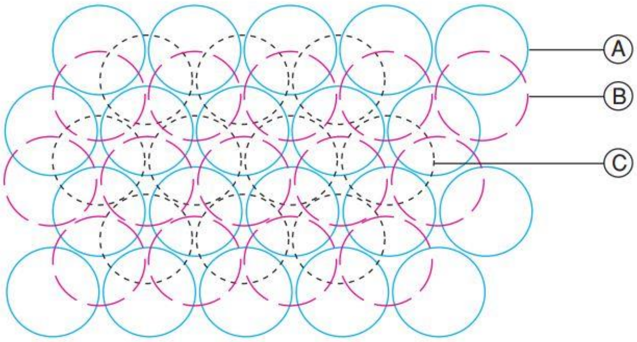


Figure 4. Cubic close-packing (ccp) with ABC layer sequence.[2]

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).

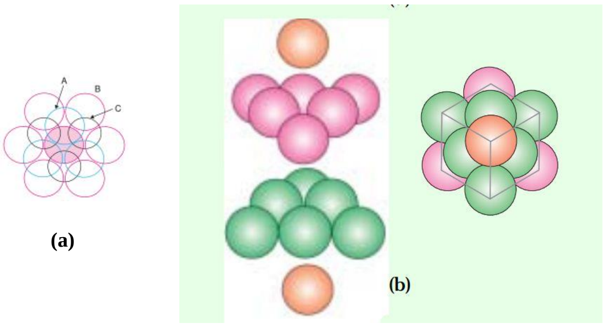


Figure 5. (a) Coordination number 12 of the shaded sphere in ccp; [2] (b) face centred cubic (fcc) formed from ccp. [4]

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.

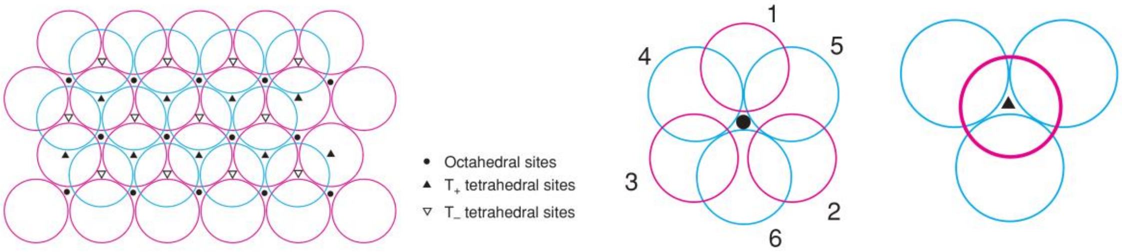
Voids in crystal: Octahedral (O) and Tetrahedral (T_+ and T_-)

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 layer A and three in layer B, as shown in Fig. 6a & 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 & 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 ccp/fcc unit cell.



a b c

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

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

It is important to visualise and understand what are 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 show in Fig. 7, a fcc/ccp unit cell that has anions, X, at corners and face centres (A, B, C, and D). The octahedral sites are easiest to locate; they are at edge-centre 1, 2, 3 and body-centre 4 positions. If the unit cell has length a, the M–X distance for octahedral sites is a/2. In order to see the T_+,T_- sites clearly, it is convenient to divide the unit cell into eight minicubes by bisecting each cell edge (dashed lines). These minicubes contain anions at only four of the eight corners; in the middle of each minicube is a tetrahedral site, either T_+or T_-.

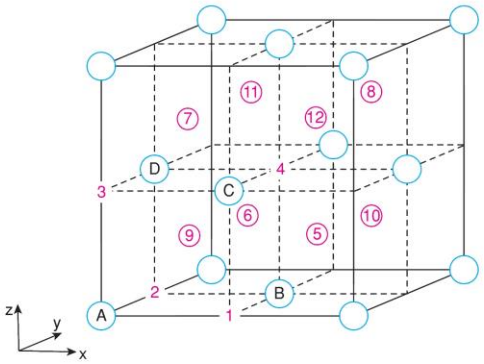
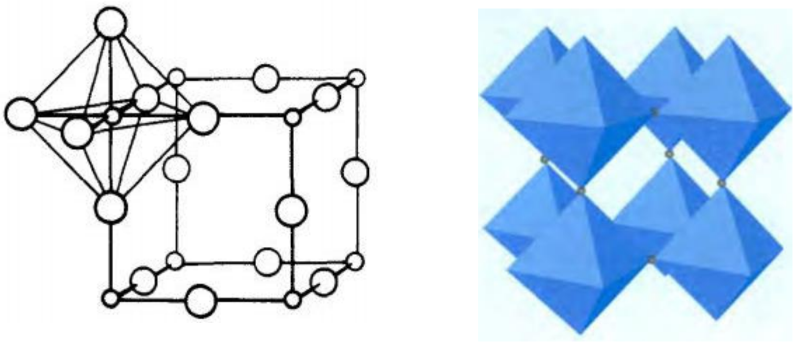


Figure 7. Available void/sites, 1–12, in an fcc/ccp array.[2]

ReO_3 Structure

It is a primitive cube structure consisting of 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.

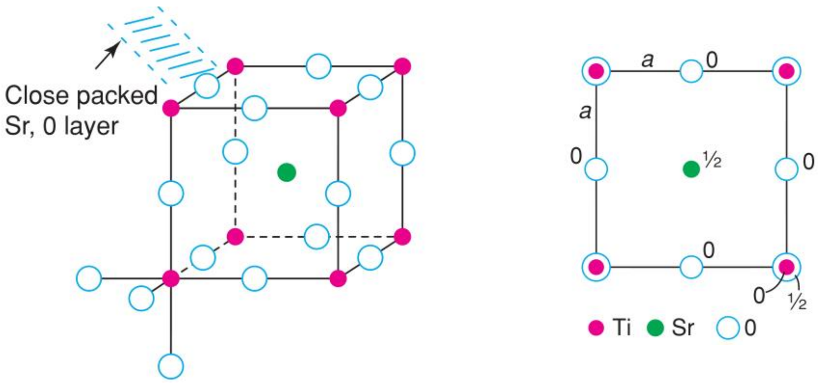


A B

Figure 8. a) ReO_3 structure;[2] b) ReO_3 structure showing the linking of [ReO_6] octahedra.[3]

The Perovskite Structure: Through ReO_3 structure and CCP/FCC & voids

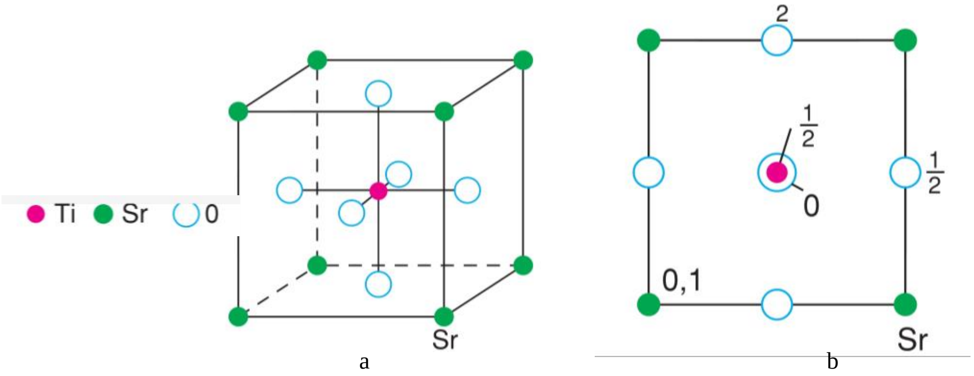
Perovskite has primitive cubic unit cell and octahedral framework as ReO_3 based on BX_6 octahedra. With an A atom added in at the centre of the unit cell of ReO_3 we will get perovskite structure. For example- $SrTiO_3$ as shown in Fig. 9a, with Sr atoms occupying the body center (½,½,½) , Ti atoms occupying cube corners (0,0,0) and oxygen atoms occupying edge centers (½,0,0; 0,½,0; 0,0,½). The 3D and 2D-view of $SrTiO_3$ structure are shown in Fig. 9a & b. O has two Ti as its nearest cationic neighbors, whereas Sr is coordinated with 8 Ti atoms and 12 oxygen atoms.



a b

Figure 9. $SrTiO_3$ structure a) 3D-view; b) 2D-view.[2]

$SrTiO_3$ can also be represented as a ccp/fcc array Sr & 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 show Fig. 10a & 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.



a b

Figure 10. Translated view of $SrTiO_3$ structure a) 3D-view; b) 2D-view.[2]

Perovskite is also regarded as a framework structure with corner-sharing 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.

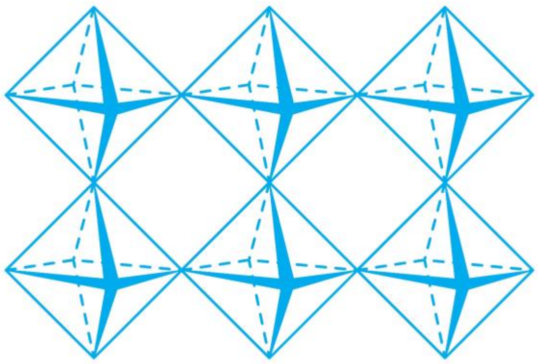


Figure 11. $SrTiO_3$ as corner sharing octahedral framework structure.[2]

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 & Sons.
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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, $CaTiO_3$; 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 $BaTiO_3$, some are anti-ferroelectric, for example, $PbZrO_3$ and $NaNbO_3$, and ferromagnetic ($LaCo_{0.2}Mn_{0.8}O_3$ and anti-ferromagnetic ($GdFeO_3$, $LaFeO_3$, etc.) compounds are known.

Table 1. Compounds with the perovskite type of structure [1]

Ideal cubic structure	$SrTiO_3$, $SrZrO_3$, $SrHfO_3$, $SrSnO_3$, $SrFeO_3$ $BaZrO_3$, $BaHfO_3$, $BaSnO_3$, $BaCeO_3$ $EuTiO_3$, $LaMnO_3$
At least one form with distorted small cell (a = 4 Å): Cubic (C) Tetragonal (T) Orthorhombic (O) Rhombohedra1 (R)	$BaTiO_3$ (C, T, O, R) $KNbO_3$ (C, T, O, R) $KTaO_{.3}$ (C, ?) $RbTaO_3$ (C, T) $PbTiO_3$ (C, T)
Distorted multiple cells	$CaTiO_3$, $NaNbO_3$, $PbZrO_3$ $PbHfO_3$, $LaCrO_3$

	low-$PbTiO_3$ low-$NaNbO_3$, high-$NaNbO_3$

In order to understand the distortions from the ideal cubic structure these oxides 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 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 (O^{-2}, halogens etc.).

$r_A + r_x = \sqrt{2(r_B + r_x)}$-------------------------------(1) [1]

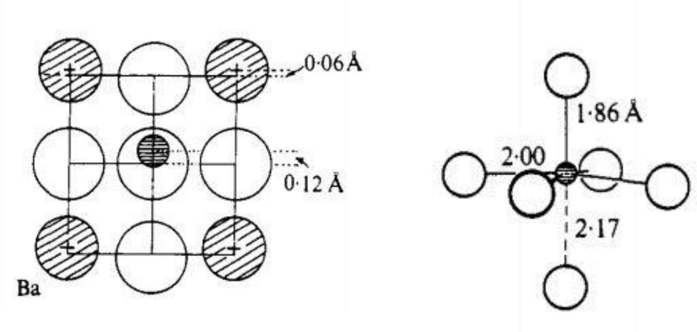
Actually the cubic perovskite structure or slightly deformed variants of it are found for ions which do not obey this relation exactly, and this was expressed by introducing a 'tolerance factor', the ratio of ionic sizes that perovskite architectures can tolerate is indicated by the Goldschmidt tolerance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

$r_A + r_x = t\sqrt{2(r_B + r_x)}$-------------------------------(2) [1]

$Tolerecne\ Factor, t = \frac{r_A + r_x}{\sqrt{2(r_B + r_x/2)}}$--------------------------------------(3) [5]

In practice, there is some flexibility over bond lengths and usually, a cubic perovskite forms with t in the range 0.9<t<1.0.

For t>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 $BaTiO_3$, t=1.06 as shown in Fig. 12a. The shifts of Ti and Ba are conventionally shown relative to the O_6 octahedra around the original Ti position. In $BaTiO_3$ 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 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 $BaTiO_3$.



a b

Fig. 12 Distorted $BaTiO_3$ structure with t=1.06 a) 2D view; b) distortion in Ti octahedra. [1]

For smaller tolerance factors, $0.85<t<0.90$, several different kinds of structural distortions occur, as in $GdFeO_3$, the A cation is too small for its site. These distortions generally involve tilting and rotation of the 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.

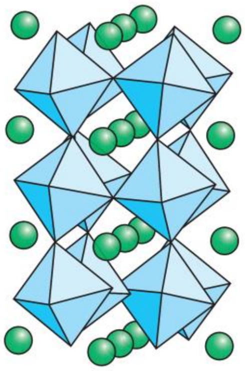


Figure 13. $GdFeO_3$ structure with $0.85<t<0.90$ showing tilting of the BO_6 octahedra.[2]

The fact that the structures of compounds 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 $AFeO_3$ (A = lanthanide) all have perovskite-type structures this is true for $AMn^{3+}O_3$ only if A is La or Ce-Yb. The compounds in which A= Ho-Lu adopt a new hexagonal structure with 5- and 7-coordination of Mn and A respectively.

Structure of Hybrid Organic-Inorganic Perovskite (HIOP)

Hybrid organic–inorganic perovskites (HOIPs) are a subclass of ABX_3 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 $MAPbX_3$ (MA = methylammonium and X = Cl, Br or I) as shown in Fig. 14

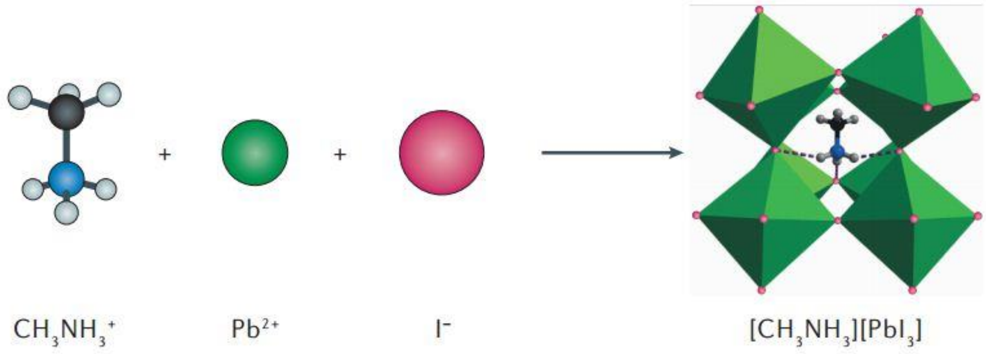


Figure 14. HOIP with an organic cation at the A-site, $MAPbI_3$ (orthorhombic, MA = methylammonium) [5]

By extending the X-site from a single halide to bridging molecular linkers, such as azide (N_3^-), cyanide (CN^-) and borohydride (BH_4^-), 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 the X-sites are $HCOO^-$ or $N(CN)^{2-}$ linkers, respectively.

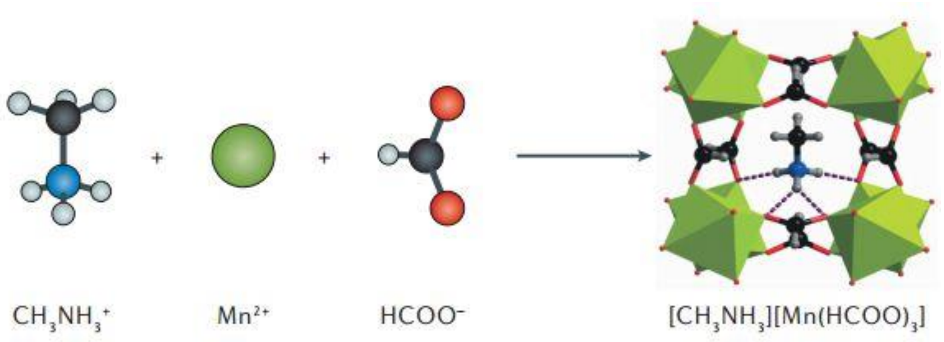


Figure 15. HOIP with an organic cation at the A-site and an organic anion at the X-site (a metal–organic framework perovskite), $[MA][Mn(HCOO)_3]$ (orthorhombic). [5]

The abundant variations of 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 3-D perovskites the size of the organic A cation is limited by the size of the 3-D 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 $t \approx 1$. Empirically it is found that $0.8 \leq t \leq 0.9$ for most cubic perovskites, although there is a slightly expanded range for distorted structures. Using t=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 of ~0.8–1.0 as shown in Table 2.

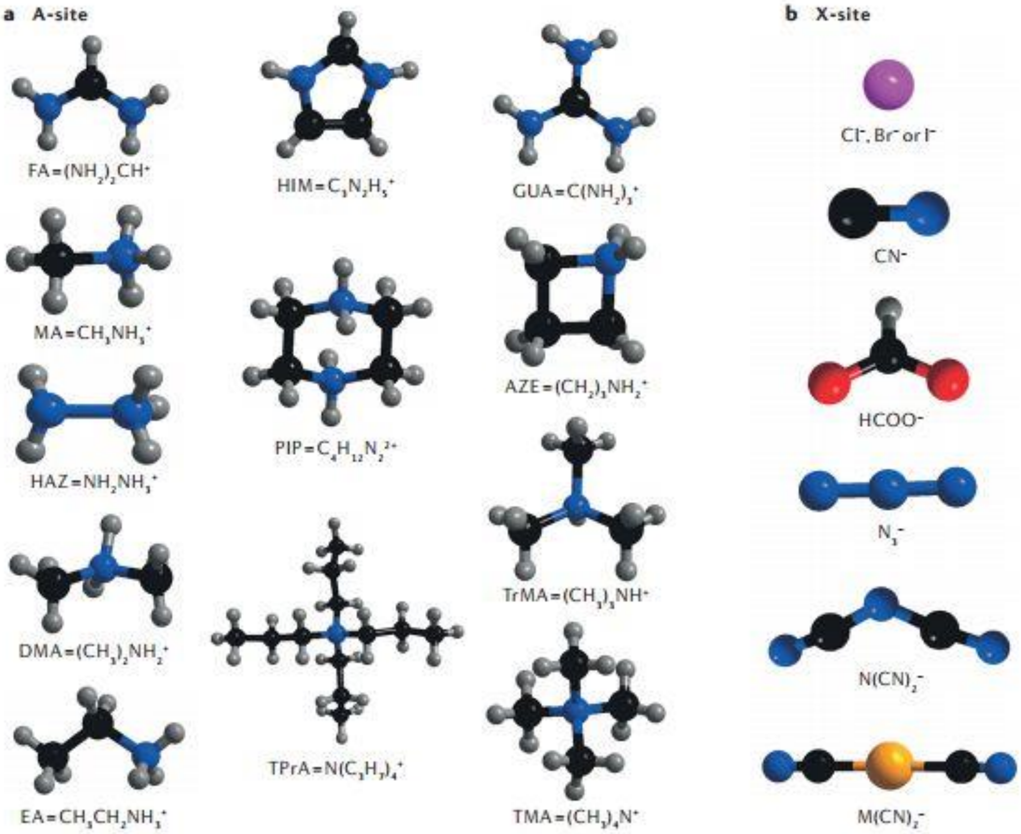
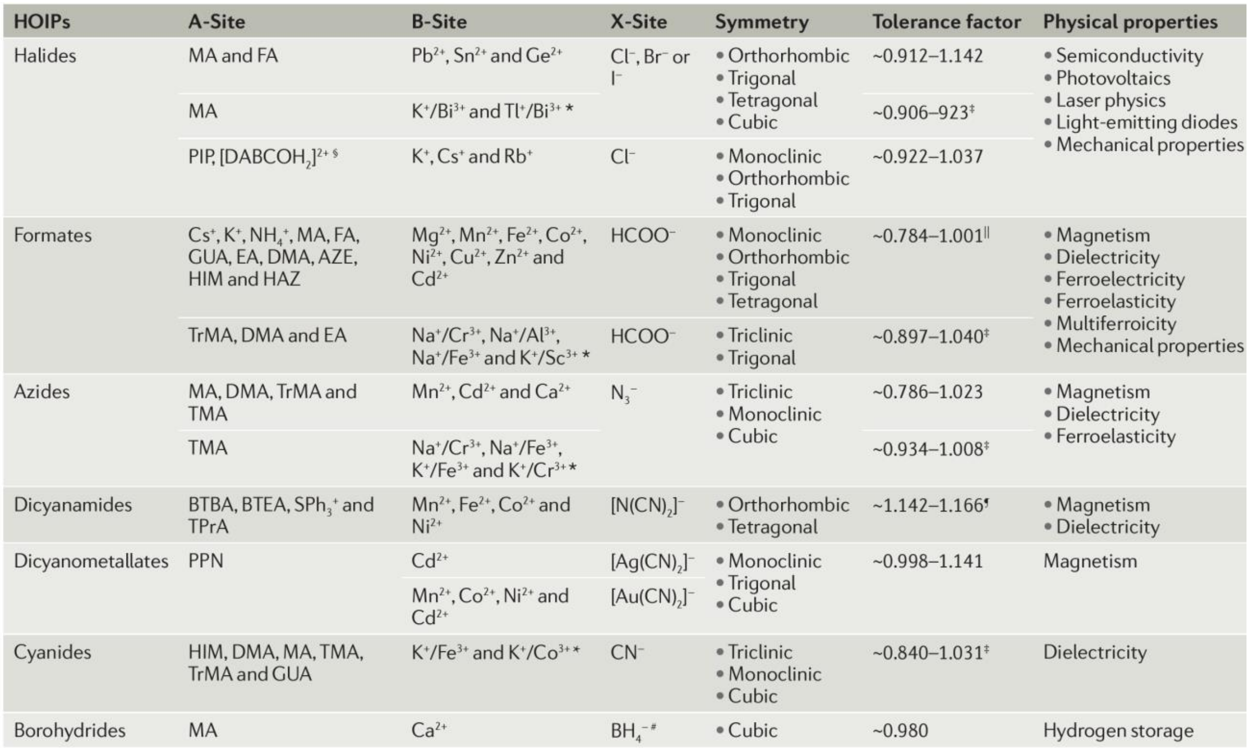


Figure 16. a) The structures of a selection of possible A-site cations used in (HOIPs); b) The structures of a selection of possible X-site anions used in HOIPs. [5]

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.

Table 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	Physical properties
Halides	MA and FA	Pb^{2+}, Sn^{2+} and Ge^{2+}	Cl^-, Br^- or I^-	• Orthorhombic • Trigonal • Tetragonal • Cubic	~0.912–1.142	• Semiconductivity • Photovoltaics • Laser physics • Light-emitting diodes • Mechanical properties
	MA	K^+/Bi^{3+} and Tl^+/Bi^{3+} *			~0.906–923‡	
	PIP, $[DABCOH_2]^{2+}$ §	K^+, Cs^+ and Rb^+	Cl^-	• Monoclinic • Orthorhombic • Trigonal	~0.922–1.037	
Formates	Cs^+, K^+, NH_4^+, MA, FA, GUA, EA, DMA, AZE, HIM and HAZ	Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}	$HCOO^-$	• Monoclinic • Orthorhombic • Trigonal • Tetragonal	~0.784–1.001$^{‖}$	• Magnetism • Dielectricity • Ferroelectricity • Ferroelasticity • Multiferroicity • Mechanical properties
	TrMA, DMA and EA	Na^+/Cr^{3+}, Na^+/Al^{3+}, Na^+/Fe^{3+} and K^+/Sc^{3+} *	$HCOO^-$	• Triclinic • Trigonal	~0.897–1.040‡	
Azides	MA, DMA, TrMA and TMA	Mn^{2+}, Cd^{2+} and Ca^{2+}	N_3^-	• Triclinic • Monoclinic • Cubic	~0.786–1.023	• Magnetism • Dielectricity • Ferroelasticity
	TMA	Na^+/Cr^{3+}, Na^+/Fe^{3+}, K^+/Fe^{3+} and K^+/Cr^{3+} *			~0.934–1.008‡	
Dicyanamides	BTBA, BTEA, SPh_3^+ and TPrA	Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+}	$[N(CN)_2]^-$	• Orthorhombic • Tetragonal	~1.142–1.166¶	• Magnetism • Dielectricity
Dicyanometallates	PPN	Cd^{2+}	$[Ag(CN)_2]^-$	• Monoclinic • Trigonal • Cubic	~0.998–1.141	Magnetism
		Mn^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+}	$[Au(CN)_2]^-$			
Cyanides	HIM, DMA, MA, TMA, TrMA and GUA	K^+/Fe^{3+} and K^+/Co^{3+} *	CN^-	• Triclinic • Monoclinic • Cubic	~0.840–1.031‡	Dielectricity
Borohydrides	MA	Ca^{2+}	$BH_4^{-\#}$	• Cubic	~0.980	Hydrogen storage

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, hybrid organic–inorganic perovskites; MA, methylammonium; PIP, piperazinediium; PPN, bis(triphenylphosphoranylidene)ammonium; SPh^{3+}, triphenylsulfonium; t, tolerance factor; TMA, tetramethylammonium; TrMA, trimethylammonium.

Suggested Reading Resources

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A_2BO_4-Layered Perovskite: The K_2NiF_4 structure

The K_2NiF_4 structure may be regarded as alternating layers of perovskite and rock salt structures, as shown in Fig. 17. The formula K2NiF4could be written in expanded form as $KNiF_3$.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 andc=1/2. 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 blocks.

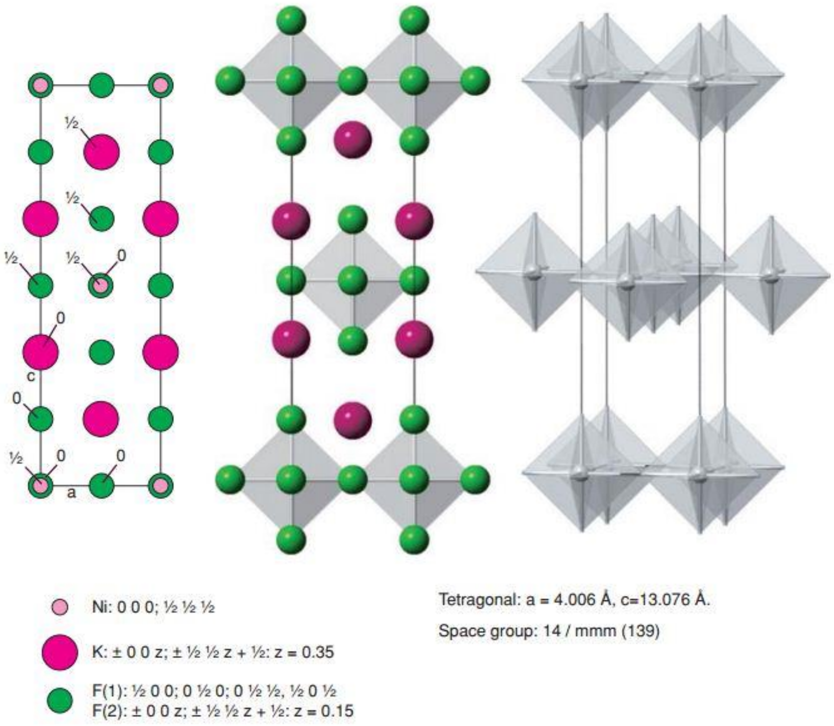

Figure 17. A_2BO_4-Layered Perovskite: The K_2NiF_4 structure.[2]

Double Perovskite $A_2BB'O_6$: Sr_2FeMoO_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_2FeMoO_6 is one such example as depicted in Fig. 18. Intervening oxygen bridges every B′ and B″ atom pair, thus forming alternating $B'O_6$ and $B''O_6$ octahedra.

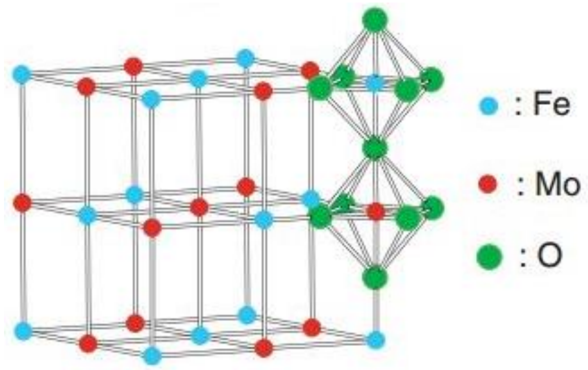

Figure 18. Double perovskite $A_2 BB'O_6$: The Sr_2FeMoO_6 structure.[6]

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CHAPTER 3

APPLICATIONS OF PEROVSKITES

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 point 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 a promising candidate in magnetic device applications.

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 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 scan lift the degeneracies between the e_g and t_{2g} orbitals further to reach an energy occupation configuration.

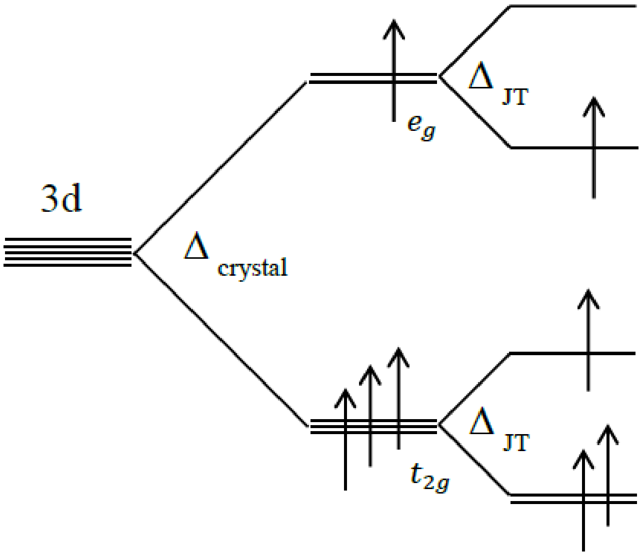

Figure 1: Schematic representation of crystal field splitting of five-fold degenerate atomic 3*d*-orbitals into and levels and further splitting is due to the Jahn-Teller (JT) distortions.

Perovskites in Magnetocaloric effect based magnetic refrigerators

Magnetic refrigeration is a cooling technology based on the magnetocaloric effect. This technique can be used to attain extremely low temperatures, as well as the ranges used in conventional refrigerators**.** The magnetocaloric 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 ΔS_m 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 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 ta 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 temperature, especially near room temperature.

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 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 perovskite 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."

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 now 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 photoconductor, 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 photoconductor. This new crystal structure combines the advantages of both ferromagnets, whose magnetic moments are aligned in a well-defined order, and photoconductors, 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 much weaker than a laser pointer—is enough to disrupt, or "melt" the material's magnetic order and generate a high density of travelling electrons, which can be freely and continuously tuned by changing the light's intensity. The timescale for shifting the magnetic in this material is also 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.

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CHAPTER 4

HYBRID ORGANIC INORGANIC PEROVSKITES

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 Bacquerel. In 1873, photoconductivity 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 ~23% in 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.

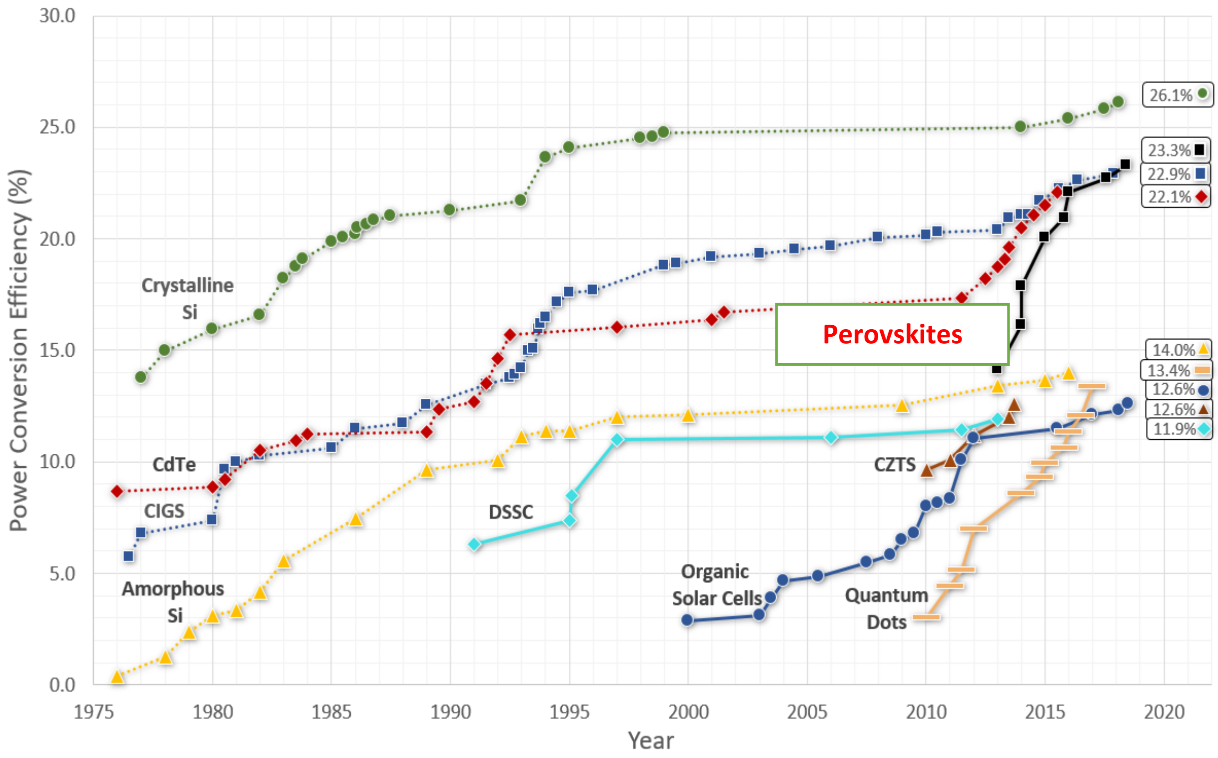

Fig.1. Values of the efficiency versus time plot for various (crystalline Silicon, CdTe, DSSC, organic solar cells. Perovskite solar cells have increased in power conversion efficiency at a phenomenal rate compared to other types of photovoltaics. [reproduced from Ref [1]].

Fig.1b Illustrates the rapid increase in the efficiency of perovskite solar cells. The increase achieved in the past four to five years is remarkable. The cells have already achieved documented efficiencies of the order of >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: solar to electrical power conversion efficiency of the best cells at the 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 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 stepwise injection of a solution of the precursors in DMF and precipitation in toluene.

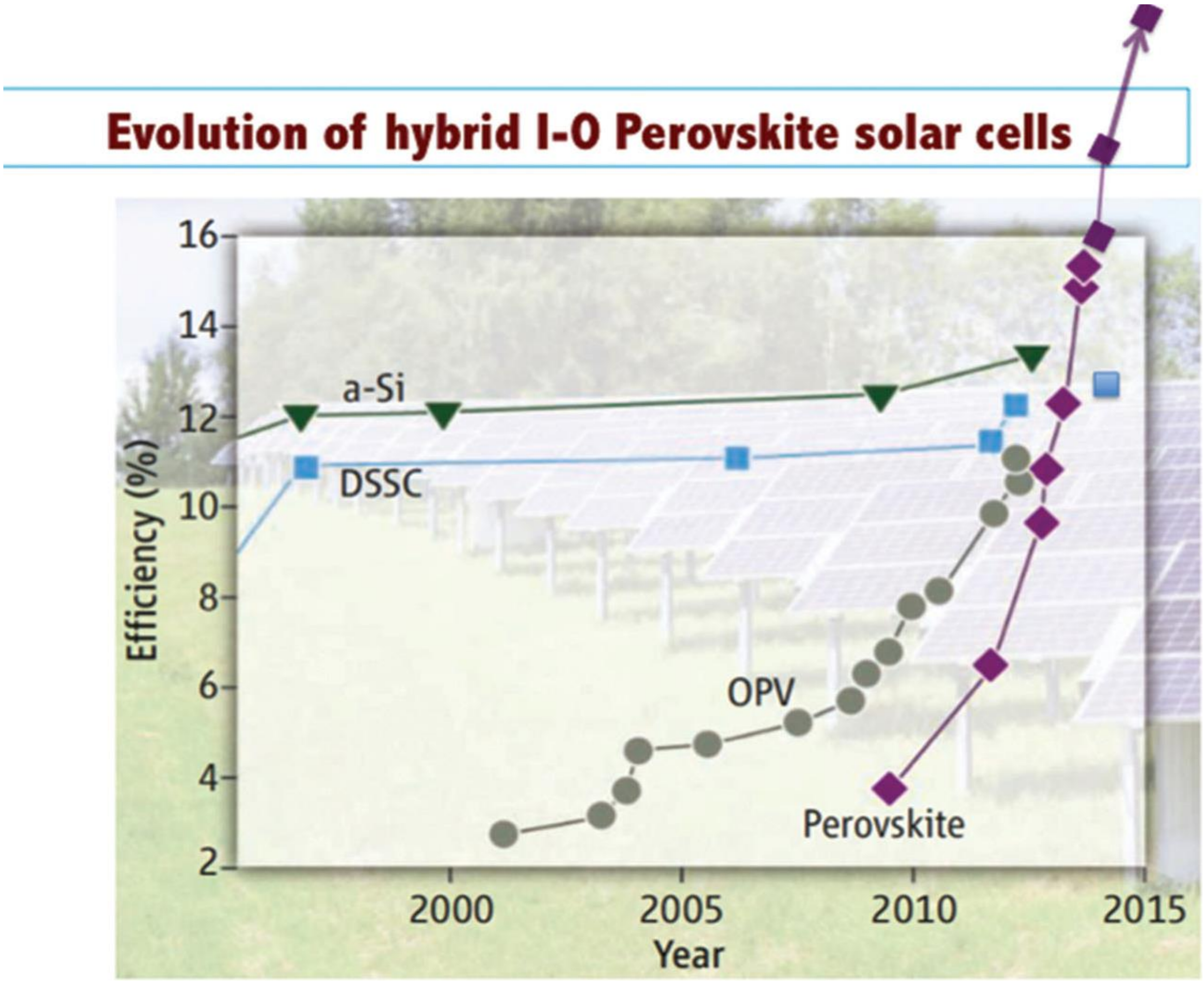

Fig.1b Typical solar cell efficiency for chosen systems with respect to the period. [reproduced from ref.7.]

Vapour assisted solution process consists of crystallization of metal halide coated substrate which is pin coated beforehand 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 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 [reproduced from

Material	Diffusion length (µm)	Carrier life time (µs)	Mobility (cm^2 V^{-1} s^{-1})	Effective mass (m$_0$)	Trap density (cm^{-3})
$CH_3NH_3PbI_3$ Poly crystalline film	0.1-1	0.01-1	1-10	0.10-0.015	10^{15}-10^{16}
$CH_3NH_3PbI_3$ single crystal	2-8	0.5-1	24-105	-	(1-3)X10^{16}
$CH_3NH_3PbBr_3$ polycrystalline	0.3-1	0.05-0.16	30	0.13	-
$CH_3NH_3PbBr_3$ Single crystal	3-17	0.3-1.	24-115	-	(0.3-6)x 10^{10}
Silicon e^-h^+	1.0 600	~1.000	1450 500	0.10 0.16	10^5- 10^{15}
GaAs e^-h^+	7 1.6	~0.01-1	8000 400	0.063 0.076	-

Table 2 Structural phase transitions for commonly employed hybrid perovskites

Composition	Phase	Temp (K)	structure	Space group	Band gap (eV)	Volume (A^3)
$MAPbI_3$	Alpha Beta Gamma	400 293 162-172	Tetragonal Tetragonal Orthorhombic	P4mm I4m Pna2	1.51-1.55	251.6 900 959.6
$MAPbCl_3$	Alpha Beta Gamma	178.8 172.9-178.8 <172.9	Cubic Tetragonal Orthorhombic	Pm3m P4/mmm P222		182.2 180.1 375
$MaPbBr_3$	Alpha Beta Gamma Delta	>236.9 155.1-236.9 149.5-155.1 <144.5	Cubic Tetragonal Tetragonal Orthorhombic	Pm3m I4/mcm P4/mmm Pna2		206.3 819.4 811.1
$MaSnI_3$	Alpha Beta	293 200	Tetragonal Tetragonal	P4mm I4cm		241.9 952.3
$FAPbI_3$	Alpha Beta	293 150	Tetragonal Tetragonal	P3m P3	1.43-1.48	768.9 2988.4
$FASnI_3$	Alpha	340	Orthorhombic	Amm2		507.03

	Beta	180	orthorhombic	Imm2		1959.2

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.

Perovskite structure is usually adopted by ABO_3 types of oxide materials. Hybrid organic inorganic perovskites with the composition ABX_3 where A and B are mono and bivalent cations and X can be monovalent anion and A cation is an organic component.

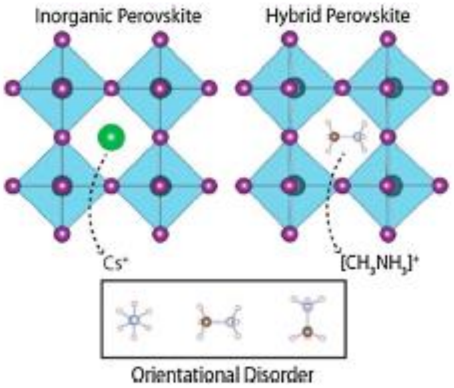

Fig. 2. Orientational disorder associated with the non-spherically symmetric organic methylammonium [(CH_3NH_3)} cation as compared to the spherically symmetric inorganic cation [Reproduced from reference 6]

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CHAPTER 5

PERSPECTIVES ON PEROVSKITES

INTRODUCTION

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 candidates [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 coprecipitation, 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 optoelectronic 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.

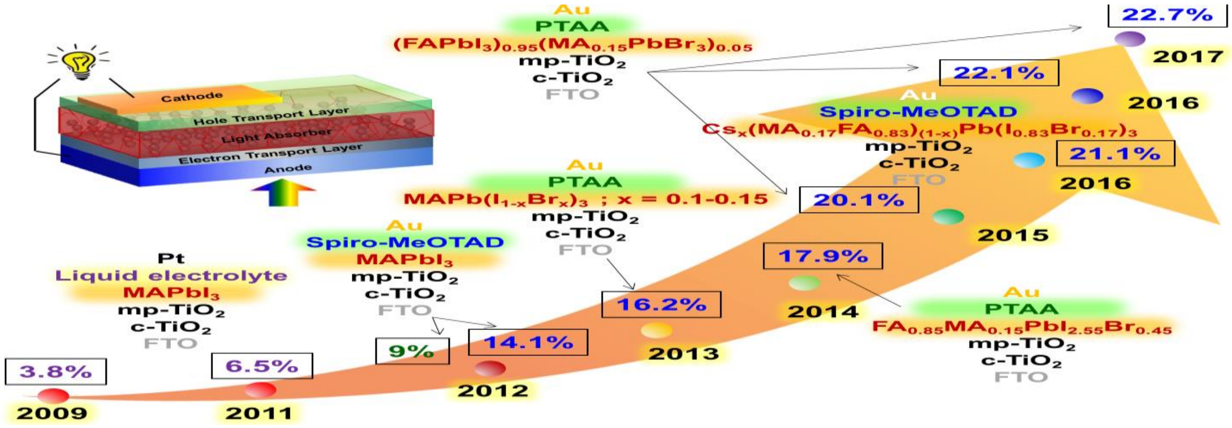

Fig X.1. The graphical representation of the year-wise evolution of the efficiency of perovskite-based solar cells. The figures in blue are the certified efficiencies by NREL. [Figure reproduced from reference 6]

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.
- 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 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 optoelectronic 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 optimised 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 behaviour of the materials and also moisture stability and all these aspects have to be carefully overcome so that commercialisation 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 application.

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