

Perovskite Materials, Synthesis and its Applications - A Review

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ABSTRACT

This article review the structure , properties, synthesis and advantages of perovskite material .The general formula of perovskite materials may be written as ABX_3 , where A = large cation, B = small cation , X = Oxygen or halogen atom, having distinct physical properties. They are useful in high value to absorption coefficient , ambipolar charge transfer, specific high dielectric constant, low value of exciton and binding energy, magento resistant properties, ferroelectric features, dielectric, piezoelectric character , wave guided and biosensors etc. Besides all these application, it has most promising optoelectronic device in the direction of commercialization, because the efficiency has been comparable to that of crystal silicon solar cell.s

Keywords: Perovskite materials, Solar Cell, and Optoelectronic devices

I. INTRODUCTION

Perovskites are not a new material ; research dates back to 1839, when the first calcium titanate compound ($CaTiO_3$) mineral was discovered. It was named "perovskite" in honor of russian mineralogist lev perovski, referring to the material with the identical crystal structure as $CaTiO_3$. Today, in the optoelectronics community, the word "perovskite" usually refers to metal halide perovskites having the molecular formula ABX_3 ; where A represents a monovalent cation such as $CH_3NH_3^+$ (MA^+), $CH(NH_2)_2^+$ (FA^+) and Cs^+ ; B indicates di-valent metal cations viz. Pb^{2+} and Sn^{2+} ; X represents halide ions: I^- , Br^- , and Cl^- . In this structure, the larger A^+ cation is coordinated with 12 X⁻anions occupying the cuboctahedral spaces, while the smaller B^{2+} cation is coordinated with 6 X⁻anions filling the octahedral spaces [1].

Earth mantle is forms various types of perovskite structure, Under high pressure, silicate mineral olivine convert into a ring-shaped backbone structure, and high pressure it converts into a perovskite structure [2-3]. Perovskite substances have been reported to show insulator, metallic, semiconductor and superconductor activity[4]. Crystal structure of perovskite materials ABX_3 type is understand through Figure1.

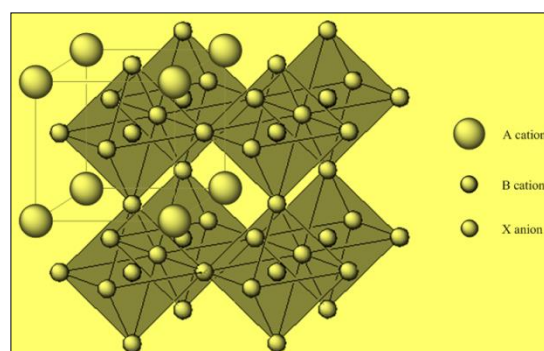


Fig1. General structure of perovskite ABX_3

Table-1 Some Oxide materials [2]

Name of materials	Examples	Applications
Perovskite	CaTiO ₃	Solar cells, opto electronics
Fluorite	CaF ₂	Fluorescence
Spinel	Fe ₃ O ₄	Ferrimagnetism
Ilmenite	FeTiO ₃	Titanium ores
Olivine	Mg ₂ SiO ₄ , Fe ₂ SiO ₄	Gemstone
Pyrochlore	(Na,Ca) ₂ Nb ₂ O ₆ F	Magnetic property
Garnet	X ₃ Y ₂ (SiO ₄) ₃	Magnetic Property
Rutile	TiO ₂	Semiconductor, Photocatalyst

Typically, cation A can be Ca²⁺, Cs⁺, organoammonium ions like methylammonium and formamidinium, etc., the cation of B site, which is smaller than the A cation, could be Ti⁴⁺, Pb²⁺, Sn²⁺, etc., and the C anion could be halide ions or oxygen. For the established of a stable cubic perovskite structure, size of the ions should meet some certain requirement, i.e. known as tolerance factor Γ defined as equation(1) should lie between $0.813 < \Gamma < 1.107$ [5,6].

$$\Gamma = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad \text{---(1)}$$

where r_A , r_B and r_X are the effective ionic radii for A, B and X ions, respectively. Now for a solar cell uses, the most used perovskite is organoammonium lead halide perovskite, for example methylammonium lead iodide (MAPbI₃), of which tolerance factor is calculated as 0.83[6].

Properties of Perovskite:

Perovskite is a close-packed structure derivative in which oxygen is situated in cubic close-packing, leaving a big volume void in space without an oxygen ion in every two layers, leaving a big volume empty in the centre. Now here the Ti⁴⁺ ion occupies at the octahedral interstices, and the large cation Ca²⁺ fills the vacant cavity created in the centre by the missing of oxide ion with a coordination number twelve. Suppose the cation of 12-coordinated is smaller than oxide ion, then the tilt of the octahedron will distort the perovskite structure. It usually takes place at a lower temperature and giving rise to many phase transformations. The corrected structure arise after tilting should be monoclinic or orthorhombic and tetragonal, or in some cases without centre of symmetry. Non-centric perovskites shown ferroelectricity, piezoelectricity and synthetic perovskites materials are used as electronic sensors[2].

Nano-crystals of Perovskite:

Perovskite materials in solar cells, their nanocrystals have also attracted significant interest. When size of crystalline semiconductors is reduced into the nanoscale, the materials can show different properties from by their bulk. Because of the quantum confinement effect, quantum dots of PbS, CdSe etc. show size-dependent band-gaps, which provide for tunable light emission by control of the particle size. As a result, these quantum dots have shown promising applications in displays and lighting[7], as well as solar cells[8]. On the basis of the facile solution processability and low trap density shown in application of solar cell of bulk perovskite materials, people have also prepared NCs of a variety of APbX₃ perovskite materials, and found promising applications, in both light emitting diodes and solar cells.

Perovskite nano crystals have shown bright and narrow-band photoluminescence that is easily tunable from ultraviolet to near-infrared wavelengths by changing either the halide composition or Nanocrystal size. Perez-Prieto and co-workers[9] reported the preparation of 6nm sized MAPbBr₃ NCs as stable colloidal solutions and made electroluminescent devices using them. Both the solutions and thin films showed bright green emission at ~530nm, and the quantum yield reached 23%. Rogach's group[10] demonstrated the size-tunable band gap of MAPbBr₃ NCs by changing the processing temperature. The emission peaks of the MAPbBr₃ NCs was tuned in region of 475-520nm when the heat was changed from 0 to 60°C, all with narrow

emission linewidths of 28-36nm, and very high quantum yields of approx 93% were achieved. Zhong et al.[10] reported the synthesis of brightly luminescent MAPbX₃ (X = Cl, Br and I) NCs with a simple ligand assisted[11]

Halide Perovskites:

Perovskites Halides are a class of materials that have shown excellent optoelectronic properties and it should be use in several applications over the last decade. The prototypical halide perovskite has a formula ABX₃ and is composed of an infinite network of [BX₆]⁴⁻ corner-connected octahedral with the A-site being located in the cubo-ctahedral voids formed by the octahedral. The A-site is typically an alkali metal or small amine, the B site is a larger divalent cation (often Pb²⁺), and the X site is a halide (Cl, Br, I). Although the halides of perovskites for a long time, and is used as an absorbing layer in solar cells first appeared in a report in 2009 by Kojima in which he will be used CH₃NH₃PbI₃ in a photovoltaic device[12]. Since the efficiency of this solar cells was increase from 4% to 25% [13]. When fabricated in the form of nanocrystals, halide perovskites were found to emit strong narrowband emission due to the quantum confinement effects on excitons in APbX₃ compounds[14-15]. Generally the derivative structures the simple halide perovskite structure as shown below in figure 2.

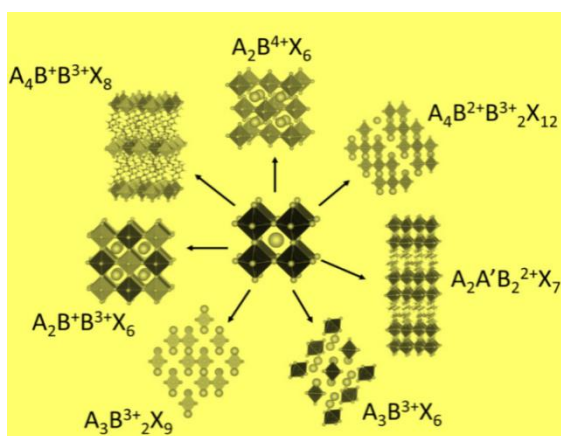


Fig 2. Some derivatives Structure of perovskite

A particularly interesting subset of perovskites, from an opto-electronic viewpoint, are the metal halide perovskites, in which the B site is occupied by a divalent metal such as Pb²⁺, Sn²⁺, Mn²⁺, Cu²⁺ or Ge²⁺ and the X sites are taken by one of the halogen ions chloride, bromide or iodide(Cl,Br,I). The size

constraints in some of the se metal halide perovskite are such that the A site can fit a relative large A-site cation such as caesium (Cs⁺) or even a small organic molecule such as methyl ammonium (CH₃NH₃) or formamidinium ((NH₂)₂CH) without violating the tolerance factor[17-18]. In the latter case,the ammonium cations are interacting with the inorganic lattice through the formation of hydrogen bonds with the halide ions to form a hybrid organic-inorganic perovskite. However, it should be noted that the difference between the ideal cubic perovskite structure depends on the relative ion sizes, and octahedral distortion and bending reduce the overall symmetry of the body, so that at room temperature many metal halide perovskites adopt a pseudocubic structure[16].

Working of perovskite solar cell: The device configuration consists of a perovskite layer sandwiched between a hole transport layer an electron transport layer. In this configuration, the incident photon is absorbed by the perovskite layer and an electron-hole pair is generated. The electron and hole move toward the selective electron and hole contacts . Finally, the electrons and holes will be collected at the corresponding contacts and deliver their energy to an external circuit.

Method of Synthesis: There are many methods for the synthesis of perovskite materials[32] but its depends upon the types of your applications.

1.Solid phase Method: It is a traditional method in this method to got perovskite oxides through lightly mixing types salts of metal which quickly convert it into sheets. After calcining at a fixed heat, this substance is obtained via grinding calcined pattern. Yuan et al. studied its magnetism, organized oxides of perovskite Y_{1-x}Gd_xFeO₃ (0 ≤ x ≤ 1) with correct lattice crystal structure with the aid of this method [23]. For this preparation procedure got the benefits of easy production method and low price, and having high material strength.

2. Sol-Gel method: In this method inorganic salts or organometallic compounds working as precursors which when hydrolysed to becomes sol and when it is condensed to obtain a gel. The minimum oxide powder is formed when it is heated . In this types of gels consist of ammonia, citric acid, ethanol, polyvinyl alcohol and so on. Using citric acid and ethylene glycol by tiny particle size. Taguchi et al. prepared LaCoO₃ [24]. Toro

et al. studied different effects of calcinations temperature[25].

3. Hydro-thermal method: By the use of aqueous solution due to the response of medium, crystals have been delivered approximately inside the response vessel underneath excessive pressure and temperature. Oxides of perovskite like LaCrO_3 , $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$, and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$, wherein the small size is among one and two μm was organized by Wang et al.[26]. The crystallinity, particle length and morphology of materials may be managed via using hydrothermal approach and put together extremely-high quality, much less agglomerated and prepared single-crystal round center-shell perovskite materials.

4. Vapor deposition method: This method is used one or various gas phase compounds or elements substances containing thin film elements to obtained thin films chemical reactions at the substrate surface. First vapor-deposited perovskite film via twin-supply evaporate PbCl_2 and $\text{CH}_3\text{NH}_3\text{I}$ at FTO materials was reported by Liu et al. [27]. Later, quite crystalline perovskite thin films have been made by means of pulsed laser deposition method[28]. A lot of researchers revealed that pleasant has a brilliant affect on the precursor ratio manage and deposition rate. Except, chemical vapor deposition, as a widely known approach, is likewise used to synthesize one-dimensional nanowires [29-30] and two-dimensional microplatelets [31].

5. Solution-chemistry method: In this method we can approaches, like anti-solvent crystallization, spin-coating, inverse temperature crystallization, are low-price and facile techniques to getting ready perovskite film and high quality crystals. Here we can use techniques of 1- and 2 -types strategies about the spin-coating technique. Inside the one-step method, perovskite precursor answer have become without delay achieved to the substrate floor and fashioned perovskite film after annealing remedy[32].

Applications of perovskite materials:

For the simplicity of structure and the flexibility of composition, perovskite based photocatalysts widespread attention for application. The recent developments of perovskite based photocatalysts for water. Besides this oxides of perovskite have a lot of applications because it shows stable structure, a large number of compounds and several properties like solar cells, Photo electrochemical cells, Thin film capacitors, Laser applications, Sensors, actuators and transducers,

Catalysts in modern chemical industry, Non-volatile memories, Ultra-sonic imaging, ultra-sonics & underwater devices, Drug delivery, Recording applications, Nonvolatile memories, Read heads in hard disks, High temperature heating applications, Spintronics devices, wireless communications microwave devices and many more, like Electrical Applications, Switching and Filtering, Catalytic properties, Intelligent Automobile catalyst, Catalyst for oxygen evolution, Cleasing Catalyst, Auto-mobile exhaust gas catalyst, Switching and Filtering, Catalytic properties, light-emitting diodes, photodetectors, lasers neuromorphic devices, artificial synapses, memristors etc. 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. In recent years, the application of ferroelectric materials in solar water splitting is another possibility to overcome the limitations of conventional semiconductors due to their special properties in the separation and transport of photoexcited charge carriers [19].

Ferroelectric perovskite materials such as BiFeO_3 and $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ generally have large, stable and tunable residual ferroelectric polarization, which can form a stable electrical polarization. This internal voltage is useful for separating photoexcited carriers and changing charge transfer direction [20–21].

Interestingly, the direction and intensity of polarization field would be tolerated by external electricity, which is utilize for solar water splitting using photoelectrodes, as the controllable surface of the ferroelectric photoelectrode allows it to function as both photocathode and photoanode. It provides the possibility of correcting the remaining polarization direction with high transmission and directs the oxidation and reduction of water solely by the ferroelectric photoelectrode. On this basis, of prepared a system of polycrystalline BiFeO_3 photoelectrodes using cost-effective spin-coating technology [22].

II. CONCLUSION

This article reviews the general structure of perovskite materials and its different novel properties and its several applications, like optoelectronic devices for example photodetectors, solar cells, lasers, light-emitting diodes and cutting-edge technologies such as neuromorphic devices like artificial synapses and

memristors and pressure-induced emission. Perovskite materials have special properties for the separation and transport of photo-excited charge carriers, the application of ferroelectric materials in solar water splitting is another possibility to overcome the limitations of conventional semiconductors and residual non-toxic and stable perovskite solar cells.

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Conflict of Interest: There is no conflict of interest.

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