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Review

Perovskite synthesis, properties and their related biochemical and industrial application

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ABSTRACT

The perovskite structure is shown to be the single most versatile ceramic host. Inorganic perovskite type oxides are attractive compounds for varied applications due to its large number of compounds, they exhibit both physical and biochemical characteristics and their Nano-formulation have been utilized as catalysts in many reaction due to their sensitivity, unique long-term stability and anti-interference ability. Some perovskites materials are very hopeful applicants for the improvement of effective anodic catalysts performance. Depending Perovskite-phase metal oxides distinct variety of properties they became useful for various applications they are newly used in electrochemical sensing of alcohols, glucose, hydrogen peroxide, gases, and neurotransmitters. Perovskite organometallic halide showed efficient essential properties for photovoltaic solar cells. This review presents a full coverage of the structure, progress of perovskites and their related applications. Stress is focused particularly to different methods of perovskites properties and there related application.

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1. Introduction

Perovskite is a yellow, brown, or black minerals, have $CaTiO_3$ as chemical formula it obtains its name from mineral named as a calcium titanium oxide and it revealed by Gustav Rose in the Ural Mounts of Russia. The name Perovskite came after Lev Perovski (1792–1856) who was the first discoverer in 1792 (Cheng and Lin, 2010). Its crystal was first described in 1926 (Wenk and Bulakh, 2004) and published in 1945 (Szuromi and Grocholski, 2017).

ABX₃ is the main formula for all Perovskite compound. In this formaula A and B are two cations of very dissimilar bulks (Atta et al., 2016), C is an octahedron ions surrounded the B ion and X is an anion that bonds to both (Schaak and Mallouk, 2000). X is often oxygen and other big ions such as halides, sulfides and nitrides are probable. Numerous oxide compounds are known belonging to a few perovskite-based homologous series (Tsunoda et al., 2003).

Perovskite oxides types (in their ideal form) are cubic or nearly cubic in structure like other transition metal oxides which contains the same formula (ABO₃). At low temperature some phase transitions may be occurs. Oxides class of compounds has wide potential for many uses due to their structures crystal which are simple and exceptional in their ferroelectric and dielectric properties.

Perovskites structures material exist in three types; the first one contain localized electrons, the second contains delocalized energy-band states, while the third can be a transition between these two types (Szuromi and Grocholski, 2017). There are several of perovskites structures types that exists in different form such as: A_2BO_4 _ Layered perovskite, ABO_3 -perovskite, $A_2A'B_2B'O_9$ _ Triple perovskite and $A_2BB'O_6$ _ Double perovskite, etc. (Thomas et al., 2017), the most abundant ones are MgSiO₃ and FeSiO₃.

In solid-state physics, perovskite oxides have been studied because they put up most of the metal ions in the periodic table due to its substantial number of different anions (Nagata et al., 2013). These types of solids are significant in the field of electrical ceramics such as; material science, astrophysics, particle accelerators (Zhu et al., 2014) geophysics, fission-fusion reactors (Nagata et al., 2013), refractories, heterogeneous catalysis environment (Sevfi et al., 2009), etc.

Oxides and oxides-like types of perovskite have different properties such as; insulator-metal transition, ionic conduction characteristics, dielectric, variation of solid-state phenomena, metallic, and superconducting characters, it also have many applications in physics and chemistry filed (Kreisel et al., 2000).

Perovskite-structured oxides can accept considerable substitutions in one or both cationic sites (A and B sites) while retaining their original crystal structures (Xu et al., 2009). Recently, perovskite-structured ceramics have several extraordinary applications such as random access memories (Pengfei et al., 2017), actuators, tunable microwave devices displays (Nenasheva et al., 2004), piezoelectric devices (Protesescu et al., 2015), transducers, wireless communications (Muralt et al., 2009), sensors, and capacitors (Kawamura et al., 2002).

In several applications perovskites proved to have great interest due to their useful properties in surface acoustic wave signal processing devices, electrochromic, switching, image storage, filtering, and photochromic (Atta et al., 2016). Recently, halide perovskites have drawn considerable attention in the fields of material exploration (Pengfei et al., 2017) due to its great effectiveness of solidstate solar.

2. Structure

Perovskite or perovskite-structure are used interchangeably. This name is given to anything has the generic form ABX_3 and the same crystallographic structure. True perovskite is formed



Fig. 1. Ideal cubic perovskite structure (ABO₃).

from oxygen, titanium and calcium, in the form CaTiO₃ (Bradley, 2017; Jeon et al., 2015). Also it referred to a kind of ceramic oxides having ABX formula. This compounds are classified into alkaline metal halide Perovskites, inorganic oxide perovskites, and organic metal halide perovskites (Chen et al., 2018).

The perovskite materials have a common structure termed as ABX₃, where "A" and "B" are cations have different sizes and "X" is an anion which bonds to both. The 'A' atoms are bigger than the 'B' atoms (Ono et al., 2017). The A and B locations may be replaced by any metal or semimetal from the periodic table. In all cases, the anion is oxygen, and can be any other could be found at this position (Chen et al., 2018).

The atomic arrangements in perovskite structure are the first found for the mineral perovskite calcium titanate, it have submetallic to metallic luster cube like-structure beside deficient cleavage and hard tenacity, colorless streak or colors include orange, black, brown, yellow and gray (Whitfield et al., 2016; Yi et al., 2019).

Ideally, the perovskite structure is described as cubic. The A atoms form the corners of the cubic cells, B atoms are in the centre in 6-fold coordination, surrounded by an octahedron of anions, the oxygen atoms are situated in the faces' centres, and the A cation in 12-fold cub- octahedral coordination.

In perovskite cubic unit cell (Fig. 1), atom A ion is a lanthanides with larger radius or alkali earth metals (Khajonrit et al., 2018). Generally, A cations are 12 fold coordinated by oxygen anions and sits in corners of the cube at corner position (0, 0, 0) while oxygen atoms are at the face center of the cubic lattice at position ($\frac{1}{2}$, $\frac{1}{2}$, 0) but tetravalent B cations lie within oxygen octahedral, occupies the body center position ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). The structure is pictured as a three dimensional network of regular corner linked BO₆ octahedral (Tan et al., 2014). The general formula as ABO_3 where, can be explained as; A and B are cations of different size and O is the anion (Zhou et al., 2018). The B atom has 6 fold co-ordination number and the A atom have 12 fold co-ordination number, the A site cation is slightly larger than B cation. Atom B is found at the cube corner position and A is at the body center while oxygen atoms are at face-centered positions (Zhou et al., 2018) but O is the oxygen ion has the ratio of 1:1:3.

Perovskite has highly stable structure, large number of compounds, variation of properties, and various applied applications. Key role of the BO_6 octahedral in ferromagnetism and Ferroelectricity. Broad formation of solid solutions lead to material optimization by structure control and phase transition engineering (Zuo and Ding, 2017). A distinctive unit cell structure of a simple perovskite compound is shown in Figs. 1–3.

The perovskite structure is stable when 0.89 $\leq t \leq$ 1.06 (taking r_0 = 0.14 nm). Ideal cubic structure only observed at room temperature when t is close to 1. If A ions are small, t < 1, and tetragonal, orthorhombic and rhombohedral deformations of structure due to rotation and tilting of the BO_6 octahedral are observed.

Some changes may exist in perovskite ideal cubic form which lead to the formation of orthorhombic, rhombohedral, hexagonal, and tetragonal forms. Generally to fulfill perovskite formation, two requirements should be exist those are electroneutrality and lonic radii requirements (Shi and Jayatissa (2018); Pandey et al., 2017).

Other types of deformations are induced by the appearance of spontaneous polarization in ferroelectric perovskites. The perovskite structure provides the building blocks for the assembly of other important crystal structures (Huang et al., 2017) such as: Roddlesden-Popper phases ($Ca_{n+1}Ti_nO_{3n+1}$), Aurivillius compounds



Fig. 2. Cubic perovskite SrTiO3.



Fig. 3. The perovskite structures and deformations.



Fig. 4. Comparison of (a) orthorhombic; (b) tetragonal and (c) cubic perovskite phases obtained from structural optimization of MAPbI3. Top row: a-c-plane and bottom row: a-b-plane (Reprinted with permission).

 $((Bi_2O_2)^{2*}(Bi_{m-1}Ti_mO_{3m+1})^{2-})$ and oxygen-deficient brownmillerite compounds (CaAlFeO_5).

Perovskite halide construction depend on three issues: (1) the constancy of the BX_6 octahedron expected by the octahedral factor m, (2) neutrality of the charges between the cations and anions, and (3) A, B and X the ionic radii are in agreement with the necessities of the Goldschmidt tolerance factor (Conings et al., 2014).

Organometallic halide perovskites include a metal cation of carbon family, an organic cation, and a halogen anion. Methylammonium-lead-iodide (MAPbI₃) is the normally used perovskite light absorber. Certain investigation substituted lead with other metal ions due to its toxicity during device construction (Tan et al., 2014; Bischak et al., 2017). In addition, several organic cations, inorganic cations and halide anions have been used to increase its stability and efficiency (Bischak et al., 2017).

Perovskite materials have different phases depending on their temperature. If temperature is lesser than 100 K, they showed a stable orthorhombic (γ) phase. On the other hand, the tetragonal (β) phase started to appear and replace the original orthorhombic (γ) phase (Bischak et al., 2017) when temperature increased to 160 K. Stable cubic (α) phase replaced the tetragonal (β) phase when temperature increases 330 K. Fig. 4 displayes all those three crystal structures (Korshunova et al., 2016).

3. Classification of perovskites

A classification of the perovskite-type structures on the basis of the radii of the constituent metallic ions has been attempted by several workers (Kuzmanovski et al., 2007). Due to the flexibility of the ABO₃ perovskite crystal structure in addition to its ability to accommodate a wide range of cations with different oxidation states.

The opportunity for several substitutions at the position of the cations is the main characteristic of perovskites (Dimitrovska et al., 2005) which lead to the occurrence of big groups of compounds with dissimilar cations in B position ($AB_xB_{1-x}O_3$); with dif-

ferent cations in A position $(A_xA_{1-x}BO_3)$; and with substitution in both cation position $(A_xA_{1-x}B_xB_{1-x}O_3)$.

A and B cations valences are generally close to 2^+ and 4^+ ; respectively, but in some cases their valences will be 3^+ for both elements only if the B^{3+} cation has a six coordination. The oxide phases have been mainly divided into two types (Galasso, 2013), and the detailed classification is shown in flowchart given in Fig. 5

- Ternary oxide ABO₃ type and their solid solutions which on the basis of oxidation states can be classified into A¹⁺B⁵⁺O₃, A²⁺B⁴⁺O₃, A³⁺B³⁺O₃ and oxygen and cation deficient species (Galasso, 2013)
- 2. Newer complex type compounds $(AB'xB''y) O_3$ where B' and B'' are two different elements in different oxidation states (Bhalla et al., 2000) and x + y = 1.

The buckling of the $(AO3)^{4-}$ layers courses in the perovskite structures due to distortion or displacement of the oxygen anion array which caused by the valence variation at the A cation position (Pengfei et al., 2017). This buckling lead to distortion of the octahedra with B cations at the centers, in this case B cation must have the flexibility to tolerate this effect (Huang et al., 2016). For filling the B cation position, the transition metal elements are the most suitable candidates due to its multi valency or the special 3d and 4d electron configurations. This is the reason that transition metal oxides have perovskite-type structures and they usually have extraordinary physical properties (Niu et al., 2015).

Compounds of perovskite complex type, A $(B_x'B_y'') O_{3}$, can be divided into four subgroups (Modeshia and Walton (2010)):

- (a) Compounds with oxygen deficient phases, A $(B_x'B_y'') O_{3-z}$.
- (b) Others which contain equal amounts of the two B elements only, A $(B'_{0.5}B''_{0.5})$ O_3
- (c) Those in which contain the higher valence state element are twice in value than the lower valence state element, A $(B'_{0.33}B''_{0.67})$ O₃,



Fig. 5. Classification of perovskite structure flowchart.

(d) Those which contain the higher valence state element in twice values as much as lower valence state element, A $(B'_{0.6}7B''_{0.33}) O_3$,

4. Properties

Perovskite materials exhibit many interesting properties due to its characteristic chemical nature such as; their non-stoichiometry of the anions and/or cations, the valence mixture electronic structure, the distortion of the cation configuration, and the mixed valence (Kim et al., 2005).

The possibility of Perovskite to synthesizing multicomponent by partial substitution of cations in positions A and B gives rise to various complex types with peculiar properties such as; Dielectric properties, Optical properties, Ferroelectricity, Superconductivity, Piezoelectricity, Multiferroicity, Colossal magneto-resistance (CMR) and Catalytic activity(Kim et al., 2005).

4.1. Dielectric properties

Dielectric materials are the materials in which electro-static fields can persevere for a long time (Niu et al., 2015). It showed a great resistance to electric current channel below the action of the applied direct current voltage and diverge sharply in their simple electrical properties from conductive materials. Layers of these substances are generally inserted into capacitors to improve their performance, and the term dielectric refers to this application (Xiao et al., 2011).

Great dielectric permittivity or ferroelectric materials are of massive importance as electroceramics for engineering and electronics industry. Ferro-electricity is generally described by a soft-mode model (Hoefler et al., 2017). Several routes have been pursued to explain the dielectric and mechanical properties starting from the simple structure BaTiO₃ by the solid solution system Pb (Zr,Ti)O₃ to other distinct families of materials. These routes

care about the flexibility of chemical manipulation and submissiveness of the perovskites (Bhatti et al., 2016).

Relaxor ferroelectric is one of the routes, which show some effects because of the to slow reduction processes for temperatures above a glass transition (Xiao et al., 2011) such as; big dielectric constants, a marked frequency dispersion and difference in dielectric constant (Kim and Yoon, 2000).

General examples for relaxor ferroelectrics are lead lanthanum zirconate titanate (PZT) and lead magnesium niobate (PMN). Ferroelectrics can be considered as ferroelectric crystals (Zheludev, 2012) and both of its high dielectric constant and low dielectric loss make perovskites one of the best candidates for tunable microwave device applications and dynamic random access memory (DRAM) (Dongling et al., 2012).

4.2. Optical properties

Perovskites have provide very special class of materials with excellent optical and photoluminescence properties. Studying the optical properties of single domain crystals of BaTiO₃ at various temperatures (Ohta and Hiramatsu (2018)) showed that the refractive index of the crystal was nearly a constant value (2.4 from 20° to 90 °C & reached 2.46 at 120 °C) (Zhang et al., 2017). The single crystal of BaTiO₃, 0.25 mm thick was found to transmit from 0.5 μ to 6 μ . The optical coefficient of strontium titanate single crystals was obtained from 0.20 μ to 17 μ in wavelength (Xin et al., 2019).

The optical density of $CaTiO_3$ showed absorption characteristics quite similar to those of $SrTiO_3$ crystals with the exception that the absorptions are shifted to shorter wavelengths (Zhang et al., 2008). Both of these compounds have been considered for high temperature infrared windows. SrTiO3 is considered as an excellent material for use with optically immersed infrared detectors (Jia et al., 2003).

Some perovskites electro-optic coefficients of are nearly constant with temperature (Pinel et al., 2004). Potassium tantalate niobate (KTN) is one of the perovskite oxides which has a large room temperature electro-optic effect and wide-angle fast optical beam scanner, therefore this type is not only useful to optical communications, but also to various other products that use optical beams, such as laser application.

Using of perovskite laser host materials is a great deal. Luminescent properties of all uncommon earth ions in perovskite-type oxides are highly stable and can work in various environments (Wang et al., 2008) in addition to they conceded to be the best candidate in field plasma display panel (PDP) devices and emission display (FED) because they are suitably conductive to release electric charges stored on the phosphor particle surfaces (Neeraj et al., 2004). Phosphors of rare earth ions doped perovskite type oxides (Dhahri et al., 2014) could be widely used in displays, X-ray phosphors.

One of the environmental friendly photoluminescence (PL) is $BaZrO_3$ which emits light in the visible region and prepared easily at low cost (Di et al., 2018; Yagi, 2009). The property of PL makes it promising for applications such as; scintillators, solid state lightning, field emission displays, green photocatalyst and plasma displays (Sayyadi-Shahraki et al., 2017).

4.3. Ferroelectricity

Ferroelectricity is the phenomenon that occurs when an external electric field is applied to some materials leading to a spontaneous electric polarization (Retot et al., 2008; Cross, 2011). The discovery of ferroelectricity in perovskite-based materials and other barium titanate (BaTiO₃) opened up new different application for ferroelectric materials, leading to significant interest in other types of ferroelectrics (Morris, 2018; López-Juárez et al., 2011).

The ferroelectric materials have dielectric constant twice larger in magnitude than those in ordinary dielectric. BaTiO3 is a wellknown ferroelectric material with relative dielectric constant, its crystal at room temperature, exhibits no net polarization, in the absence of an external field, even though the dipoles of adjacent unit cells are aligned (Xu, 2011).

Ferroelectric property is used to several purposes such as; in ultrasound imaging devices, fire sensors, infrared cameras, vibration sensors, tunable capacitors, memory devices, RAM and RFID cards, input devices in ultrasound imaging, and a. make sensors, capacitors, memory devices, etc. (Raghavan, 2015).

4.4. Superconductivity

Certain materials once cooled under a specific serious temperature exhibited zero electrical resistance and expulsion of magnetic flux fields this phenomena called Superconductivity (Kittel, 2005).

The oxide perovskites structure type provides an excellent structural framework due to the existence of superconductivity. Perovskites which have Cu act as high-temperature superconductors. The first reported example of superconducting perovskites is La-Ba-Cu-O perovskite and there are many more (Mourachkine, 2004). Perovskite oxides now eclipsed the use of Intermetallic compounds as source of many superconducting materials such as; cesium tungsten bronzes and Sodium, potassium, rubidium (Cava, 2008).

Type 2 group Superconducting "perovskites" metal-oxide ceramics are those compounds which have specific ratio of 2 metal atoms to every 3 oxygen atoms (Morita et al., 2006). This type of superconductors is contained of alloys and metallic compounds (excluding for niobium, vanadium, and technetium), recently they achieve higher transition temperature than Type 1 superconductors (Ishihara (2009)).

4.5. Piezoelectricity

Some materials have the capacity to produce an electric charge in reaction to applied mechanical stress is known as Piezoelectricity (Wang et al. 2004). Therefore, if definite crystals were subjected to mechanical strain, they became polarized at a degree which is proportional to the applied strain (Wang et al., 2006). On the other hand, they have some changed when they were exposed to an electric field which is known as the inverse piezoelectric effect (Brockmann, 2009).

There is a difference between piezoelectric and ferroelectric materials, in the fires materials it requires some external impetus while in the second there is spontaneous alignment of electric dipoles by their mutual interaction. Therefore, all piezoelectric are not ferroelectric but all ferroelectrics are piezoelectric.

Some synthetic piezoelectric materials are the piezoelectric ceramics with the perovskite crystal structure (Aksel et al., 2011) having a general formula of $A^{2+}B^{4+}O^{2-3}$. Also there are naturally occurring piezoelectric materials; quartz, cane sugar, collagen, topaz, rochelle salt, tendon, etc.

Perovskites materials Piezoelectricity property have many valuable scientific application (Ye, 2008) such as; Cigarette lighter, Sensors, Microphones, High voltage and power source, Pick-ups, Pressure sensor, Force sensor, Strain gauge, Actuators, Piezoelectric motors, Piezoelectric motors, Nano-positioning in AFM, STM, Acuosto-optic modulators, Loudspeaker, Valves, Energy harvesting, AC voltage multiplier (Kleckers, 2013).

4.6. Multiferroicity

Multiferroics include special class of materials showing concurrent ferroelectric, ferromagnetic, and ferroelastic ordering. The specialty of these materials localized in their ability to simultaneous utilization of both their magnetization and polarization states, a potential which make them excellent candidates for memory devices and sensors (Spaldin et al., 2010; Ramesh and Spaldin, 2007).

Many multiferroics are transition metal oxides with perovskite crystal structure, and include rare-earth manganite and ferrites (Wang et al., 2010). These materials shows multiferroicity even at room temperature (Kézsmárki et al., 2011). Bismuth ferrite, a rhombohedrally distorted perovskite (compounds with multiferroics property) possesses both anti-ferromagnetic and ferroelectric order for a widespread temperature range which is greatly above room temperature (Singh et al., 2011).

Most of the ferromagnetic materials are generally metals and they must be an insulator because the absence of insulators limits the simultaneous occurrence of ferromagnetic and ferroelectric ordering (Ghosh et al., 2019). The important requirement for ferroelectricity is a structural distortion from the high symmetry phase that removes the center of inversion and allows an electric polarization (Fig. 6) (Zverev et al., 2014). It has been found that even in the absence of any structural distortion, magnetic spin ordering can produce ferroelectricity.

Multiferroics have great technological potential importance due to the co-occurrence of magnetic order and ferroelectric polarization joint in a single-phase material (Eerenstein et al., 2006). Multiferroic materials open promising opportunities for spintronics devices and designing novel microelectronic (Bai et al., 2005). It has been found that even in the absence of any structural distortion, magnetic spin ordering can produce ferroelectricity.

Multiferroicity, a co-occurrence of natural ferroelectric and ferromagnetic moments, is an uncommon phenomenon due to the minor number of asymmetry magnetic point groups that permit an unplanned polarization (Johnson and Radaelli, 2014).



Fig. 6. Conditions required for ferroelectricity (polarization) and ferromagnetism (unpaired electron spin motion).

Multiferroic materials classified into Type I & type II Multiferroic. Type I includes the structures with nonpolar-to-polar phase transition which responsible about the breaking of reversal equilibrium leading to ferroelectricity at high temperatures. While in type II the primary order parameter is the staggered (antiferromagnetic) magnetization (Liu et al., 2011). In addition, if the magnetic ordering goes below a given temperature, it lowers both magnetostructural coupling to the crystal structure (this gives rise to an electrically polar state) and the symmetry group from polar magnetic phase to a nonpolar parent phase making wrong ferroelectricity therefore ferroelectric order and magnetic factors are closely joined (Francis et al., 2016).

4.7. Colossal magneto resistance (CMR)

Colossal magneto resistance (CMR) is a property of particular materials (mostly manganese-based perovskite oxides) that allows them to change their electrical resistance in the presence of a magnetic field (Lu et al., 2004). The discovery of this property (CMR) affect the divalent alkaline-earth ion doped perovskite manganite $RE_{1-x}AE_xMnO_3$, where AE represents divalent alkaline earth ions (Ca, Sr, Ba) and RE is trivalent rare-earth (La, Pr, Sm, etc.) (Garg et al., 2009).

Magnetic phases are observed depending on the orbital occupancy of the manganese ions and the associated orbital order, different. In these compounds, ordering temperatures of similar magnitude for both degrees of freedom because their orbitals and spins are strongly coupled (Feroze et al., 2017).

On the other hand, magnetic frustration, low dimensionality, and quantum effects lead to very peculiar phase graphs with or without magnetic long range order. In unfulfilled lattices the degeneracy of the magnetic zero state can be frequently lifted by second order energy scale or quantum fluctuations (Tokura, 2006). Generally, CMR effect is closely related to its manganites which are correlated electron systems with interplay among the lattice spin, Jahn-Taller effect, charge & orbital degrees of freedom, electronic phase separation, charge ordering, etc. (Rojas-Cervantes and Castillejos, 2019).

4.8. Catalytic activity

Perovskites displayed exceptional catalytic action and great chemical stability therefor it includes in the catalysis of changed reactions. Also, it can be defined as an oxidation or oxygen-activated catalyst and as a model of active sites (Roni, 2018).

The perovskite structure showed high catalytic activity in addition there stability allowed the preparation of several compounds from elements with uncommon valence statuses or a great extent of oxygen lack (Roni, 2018). They also can act as motor exhaust gas catalyst, cleaning catalyst, and intelligent automobile catalyst for Table 1Some properties of perovskite oxides.

| Typical property | Typical compound | |
|-------------------------|---|--|
| Ferromagnetic | BaTiO ₃ , PdTiO ₃ | |
| Piezoelectricity | Pb(Zr, Ti)O ₃ , (Bi, Na)TiO ₃ | |
| Electrical conductivity | ReO ₃ , SrFeO ₃ , LaCrO ₃ , LaCoO ₃ , LaNiO ₃ | |
| Superconductivity | La _{0.9} Sr _{0.1} CuO ₃ , YBa ₂ Cu ₃ O ₇ , HgBa ₂ Ca ₂ Cu ₂ O ₈ | |
| Ion conductivity | La(Ca)AlO ₃ BaZrO ₃ , CaTiO ₃ , SrZrO ₃ , | |
| | BaCeO _{3,} La(Sr)Ga(Mg)O ₃ , | |
| Magnetic property | LaMnO ₃ , LaFeO ₃ , La ₂ NiMnO ₆ | |
| Catalytic property | LaCoO ₃ , LaMnO ₃ , BaCuO ₃ | |
| Electrode | La _{0.6} Sr _{0.4} CoO ₃ , La _{0.8} Ca _{0.2} MnO ₃ | |

various catalytic environmental reactions. Some Perovskite types (containing Cu, Co, Mn, or Fe) showed catalytic action to the straight decay of NO at high temperature due to the occurrence of oxygen deficiency and the simple removal of the surface oxygen in the a shape of a reaction product (Nishihata et al., 2005).

Perovskite revealed a great effect as a vehicle catalyst; intelligent catalyst, removal of CO &NO, effective catalyst and Not combusted hydrocarbons. It can show redox properties to reserve unlimited scattering state (Singh et al., 2007) and when oxidation occurs fine metal bits of Pd will formed with radius of 1–3 nm. This lead to partial replacement of Pd into and sedimentation from the structure of the perovskite under decreasing and oxidizing states showing a great scattering state of Pd. This cycle improved the long-standing reliability of Pd through the pollutants elimination from the exhaust gas. The great stability of the perovskite structure and the unlimited spreading state of Pd were the cause of calling it as intelligent catalyst (Wang et al., 2014) (see Table 1).

5. Synthesis

All the usual physical or chemical properties of perovskite oxides ceramic are used for synthesizing perovskite. Conventional ceramic methods built on solid phase reactions at high temperatures are usually used to obtain these materials (Sharm et al., 2018).

Usual synthesis of ceramics using solid phase reactions which has many drawbacks due to repeatedly ground and heated of metal oxides or the corresponding salts before calcinations (Varma et al., 2016). These drawbacks are in the form of inhomogeneity of the products, presence of defects which interferes with luminescence, incorporation of chemical impurities during repeated grinding and heating operations and coarseness of particles which makes them unsuitable for coatings (Eerenstein et al., 2006).

To improve synthesis methods and avoid these disadvantages to get pure materials several new methods have been developed (Zaharii, 2012) such as: Co-precipitation method, Solid-state reactions, Hydrothermal synthesis, Pechini method, Gas phase preparations, Sol-gel method, Low temperature solution combustion method, Microwave synthesis, PVD methods – laser ablation, MBE and Wet chemical methods (Nieto et al., 2007).

5.1. Co-precipitation method

The precipitation of metal salts is a method which is frequently used for the synthesis of simple oxides (Ecija et al., 2012). Precipitation occurs after adding a chemical reagent which decrease the solubility limit. Co-precipitation happens when different cations in solution precipitate simultaneously.

For the simultaneous precipitation of all cations and obtaining perfect homogeneous products it is essential to control the temperature, concentration, pH and solution homogeneity. Ammonia, ammonium oxalate, urea and ammonium carbonate are some of the popular reagents used for precipitation. The formation of oxide compounds, insoluble in solutions occurs due to the thermal decomposition of the hydroxides, organic or carbonates salts (Pérez-Coll et al., 2003).

5.2. Solid-state reactions

In solid-state reactions, both of the raw materials and the last products are solid therefore all reagents such as carbonates, nitrates, oxides can be mixed with the stoichiometric ratios (Shandily et al., 2016). Using solid-state reactions Perovskites can be synthesized by mixing oxides or carbonates of the B-site and A- metal ions in the perovskite formula ABO₃ at the essential proportion (Kamihara et al., 2008) and required at temperatures of >2/3 m.p. at a time up to ten hours to obtain the last product with the desired composition (Ecija et al., 2012).

All ingredients are ball milling effectively in a milling media of isopropanol or acetone. The acquired product is dried at 100 °C and left in air to calcinate for 4–8 h at 600 °C under alternating temperature (warming/cooling rates 2 °C/min). The obtained samples are ground and sieved and re-calcinated again at 1300–1600 °C for 5–15 h under the alternating temperature as before (rate is 2 °C/min) to insure the formation of single phase of perovskite. The achieved samples then grinded and sieved (Danks et al., 2016).

5.3. Hydrothermal synthesis

The hydrothermal synthesis principle of is carry out the reaction in the aqueous solution or suspense the precursors at high temperature and pressure. Crystalline powders can be obtained in this method without calcination (Esposito, 2019). This method previously used to synthesize and check the thermodynamic constancy of BaTiO₃ and other perovskites but now the particle size and shape (by using it) can be changed through controlling the reaction temperature, pH time and concentration of reactants (Miron, 2008).

Recently, BaTiO3 started to be synthesized at low temperatures using this method by using an electric field in a hydrothermal shell at specific temperatures (100 and 200 °C), after this some researcher manage to synthesized it using an electric field to further reduction of the hydrothermal synthesis temperature (Shandily et al., 2016).

5.4. Pechini method

The Pechini method, the polymeric precursor method, or the method of mixed liquids are the same name for one synthesis method (Shandily et al., 2016) which allows the synthesis of oxides, with an excellent control of the stoichiometry of reaction products and the reactants, and showed high reproducibility and homogeneity of the reaction mixture (Esposito, 2019).

The principle of this method is the construction of a chelate by the reaction of changed cations and introduced it into the system as soluble salts with a carboxylic acid (Koyanagi and Bohme, 2006). The resulting solutions containing metal salts and citric acid which when mixed with a desired ethylene glycol and heated ($80-100 \,^{\circ}$ C) gives a clear solution. Further heating to higher temperature ($150-250 \,^{\circ}$ C) leading to the occurring of condensation reaction involving COOH and OH groups, which leads furthermore leading to the formation of a polyester "resin", in which metallic cations are distributed uniformly in the resin mass (Abbas et al., 2014).

5.5. Gas phase preparations

Gas phase reaction or transport reaction used for the admission of perovskite films with a specific thickness and structure (Koyanagi and Bohme, 2006). Gas phase admission can be classified to three types of deposition at: at the crystallization temperature under suitable atmosphere (i), an intermediate temperature of 873–1073 K then post-annealing treatment (ii), and a low substrate temperature then post- annealing at high temperature (i) (Danks et al., 2016).

 $YBa_2Cu_3O_{7-x}$ films is one of the Yttrium barium copper oxide which can be made by the co-evaporation of Y, Cu, and BaF_2 then hardening at high temperatures in O_2 atmosphere and wet with water vapor to reduce the hardening time and substrate interface (Boston et al., 2014). Magnetron sputtering, Laser ablation, molecular beam epitaxy, thermal evaporation, dc sputtering, and electron beam evaporation techniques were developed for gas phase deposition (Tuan et al., 2019).

5.6. Sol-gel method

Sol-gel alkoxide route is a prominent method in the field of ceramics. Several perovskites phases were probably the first such non-silicate ceramics ever made by this techniques (Kemnitz and Noack, 2015). The metallic alkoxides are available commercially for a large variety of metals from which hybrid materials are obtained by reactions in the presence of organic compounds (Zheludkevich et al., 2005). The processing of oxide compounds by alkoxide route is based on the hydrolysis and polycondensation of metallic alkoxides (Kessler et al., 2006).

Sol gel method were usually applied to many of the aluminate, titanate, and complex mixed cation phases and broadly used to prepare nanosized materials (Sunde et al., 2016), but its application is limited due to the stability of its precursor system and it is difficult to control the chemical composition of complex oxides. Sol-gel techniques have attracted broader courtesy particularly for making thin films at low temperatures. Sol-gel procedure in aqueous medium uses inorganic salts and chelating agents of carboxylic acids or polyol as precursors (Feinle et al., 2016).

5.7. Low temperature solution combustion method

The low temperature combustion synthesis (LCS) technique is a novel time saving and energy effective method for the synthesis of ultra-fine powders (Srivastava, 2012). It is based on gelling, some organic fuel, and combustion of an aqueous solution containing salts of the desired metals, giving a voluminous fluffy product with large surface area (Wang et al., 2008).

There are several advantages of this method, so low temperature combustion synthesis has been adopted in the preparation of CaSiO3 ceramic (Popa and Calderón-Moreno, 2009).

5.8. Microwave synthesis

Microwaves are gradually used as a fresh synthetic way in solid State Chemistry. The usage of microwave irradiation is a hopeful alternative heat source for the synthesis of perovskite oxides (Alammar et al., 2017). This method offer a time savings and massive energy when compared to the other method of ceramic synthesis. Microwave synthesis of perovskite oxides can be achieved by numerous procedures such as Joining microwave heating with other synthetic techniques such as sol-gel or combustion, Irradiation of a solution in an autoclave and Direct irradiation of a mixture of the solid reactants (Prado-Gonjal et al., 2014).

There are two methods of microwave synthesis, these are microwave-assisted hydrothermal synthesis & solid-state microwave, the solid-state microwave is narrow to "simple" compositions only while the combining of microwaves with other methods such as combustion, hydrothermal synthesis, or sol-gel permits for enhanced stoichiometric control of complex doped phases (Schmidt et al., 2015).

Joining solvothermal synthesis and microwave heating result in novel morphologies and metastable phases. Perovskite oxide materials properties as superconducting, dielectric, ferromagnetic, ferroelectric, and multiferroic systems play very important rule in there synthesis using microwave techniques (Zhu, 2009). The simplicity and speed of microwave synthesis so it became attractive for Pb-containing perovskite, because it minimizes the Pb-loss (Alammar et al., 2017).

5.9. Roll of PVD methods - laser ablation, MBE

One of the most promising techniques is Pulsed-laser deposition (PLD) which is used for the creation of excellent matrixes, complex-oxide, heterostructures, and well measured interfaces. The use of a pulsed laser to make the stoichiometric changes the material from a solid source to a substrate (Christen and Eres, 2008).

PLD has been used broadly in the development of those hightemperature cuprates and many other multipart oxides, especially compounds that cannot be gained via an equilibrium route. The method has been successful for the film synthesis of Y-type magnetoplumbite. The process of laser ablation has been considered widely because of its importance in laser machining (Willmott, 2004).

5.10. Wet chemical methods (solution preparation)

Wet-chemical methods is an efficient accurate synthesis technique for synthesising the redox state of double-perovskite compound. These procedures involving the sol-gel preparation, co-precipitation of metal ions using different precipitating agents and thermal treatment (Selbach et al., 2007).

This method opened new guidelines for molecular construction in the production of perovskites, and it characterized by its simplicity, reduced sintering time, mass production, high level of repeatability, lower temperature than solid-state reactions, better flexibility in thin films forming, superior homogeneity, betterquality reactivity, improved control of stoichiometry, purity, particle size, and a low industrialization implementation cost (Taylor et al., 2019).

Wet Solution methods were categorized built on the methods used for solvent removal. Two classes for this method were recognized: the first one is one the separation of the solid & liquid phases in which first precipitation followed by filtration, centrifugation, etc. (i) while the second one is for solvent removal and in this thermal treatment such as evaporation, sublimation, combustion, etc., (ii). There are some aspects must be taken in thought in solution methods like solubility, purity, toxicity, solvent compatibility, choice of probably inert anions, and finally cost (Kumar and Chand, 2018; Tarale et al., 2013).

6. Applications

Perovskite oxides type are have wide applications due to its stable structure, large number of compounds, variety of properties (Deka et al., 2014). Inorganic perovskite type oxides are attractive nanomaterial for varied applications due to its large number of compounds, very stable structure, variety of properties and several practical applications. Some of these compounds nanomaterial are wildly applied in catalysis of many chemical engendering fields. The activity of these oxides as catalyst is better than any other transition metals and precious metal oxides.

Depending on Perovskite oxides distinct variety of properties they became useful for various applications such as; Thin film capacitors, Non-volatile memories, Photo-electrochemical cells, Recording applications, Read heads in hard disks, Spintronics devices, Laser applications, For windows to protect from high temperature infrared radiations, High temperature heating applications, Thermal barrier coatings, Frequency filters for wireless communications, Non-volatile memories, Sensors, actuators and transducers, Drug delivery, Catalysts in modern chemical industry, Ultra-sonic imaging, ultrasonic & underwater devices (Ottochian et al., 2014). Some more important applications of different perovskite structured are listed in Table 2.

Recently, they utilized in electrochemical sensing of alcohols, acetone, glucose, gases, amino acids, H_2O_2 , sensitivity, excellent reproducibility, unique long-term stability, anti-interference ability and neurotransmitters exhibiting good selectivity, etc.. In addition, some perovskites are worthy applicants for the development of effective anodic catalysts for direct fuel cells viewing high catalytic performance (Kumar and Chand, 2018). Some details of the application are summarized in the following.

6.1. Sensors and biosensors

6.1.1. Gas sensors

There are a sum of necessities that the resources used as gas devices must content such as hydrothermal constancy, good similarity with the target gases, suitable electronic structure, resistance to poisoning, and alteration with existing skills (Christen and Eres, 2008).

Perovskite oxides used as gas sensors like semiconductors, LaFeO₃ and SrTiO₃. They are interesting materials as gas sensors for their ideal band gap, thermal stability, and size difference between the cations of B-- and A sites. Perovskites materials which contain cobaltates, titanates, and ferrites were applied as gas sensors for spotting CO, NO₂, methanol, ethanol, and hydrocarbons (Taylor et al., 2019).

6.1.2. Glucose sensor

It is important to determined H_2O_2 and glucose in numerous fields in our live such as in food, pharmaceutical products and clinic. H_2O_2 is oxidizing agents in many neutrinos and industries. Glucose also is the basic metabolite in many of the living organisms and in clinical check of diabetes mellitus, and universal healthiness problem. Therefore it is important to have excellent sensitive biosensors for determination both H_2O_2 and glucose (Ottochian et al., 2014).

Although there are different types of enzymatic work as glucose sensors but these enzyme lack the stability due to its basic nature in addition its action was greatly affected by poisonous chemicals, temperature, humidity, etc. consequence, there must be searching

Table 2

Some important applications perovskite structured and their properties.

| Reference compound | Properties | Existing and potential applications | Notes |
|---|---|---|---|
| BaTiO ₃ | Ferroelectricity, high dielectric constant, | Multilayer ceramic capacitors (MLCCs), | Most widely used dielectric ceramic $T_{r} = 125 \circ C$ |
| $(\mathbf{P}_{2}, \mathbf{S}_{r})$ TiO | Non linear dielectric properties | Tunable microwaye devices | Ic = 125 C |
| $(\text{Da}, \text{SI}) \cap (\text{Da})$ | Riozooloctricity Forroeloctricity | Piozooloctric transducors and actuators | DZT: most successful piezooloctric |
| FD(Z1,11)O ₃ | riezoelectricity, renoelectricity | ferroelectric memories (FERAMs) | material |
| Bi ₄ Ti ₃ O ₁₂ | Ferroelectric with high Curie temperature | 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 | frequency-dependent properties, High permittivity, large electrostrictive coefficients, |
| SrRuO ₃ | Ferromagnetism | Electrode material for epitaxial | |
| $(I = A)MnO_{n}$ | Ferromagnetism spin-polarized electrons | Magnetic field sensors spin electronic | |
| A = Ca Sr Ba | giant magnetoresistance | devices | |
| SrTiO ₂ | Incipient ferroelectricity thermoelectric | Alternative gate dielectric material | Multifunctional material |
| 511103 | nower metallic electronic conduction | harrier laver canacitors photoassisted | Water and cronial material |
| | when n-doped mixed conduction when n- | water splitting substrate for epitaxial | |
| | doped_photocatalyst | growth | |
| LaGaO ₂ | Oxyde-ion conduction | Electrolyte in solid oxide fuel cells (SOFCs) | $BaIn_2O_5$ is an oxygen deficient perovskite |
| BaIn ₂ O ₅ | | j | with brownmillerite structure. |
| BaCeO ₃ , BaZrO ₃ | Proton conduction | Electrolyte in protonic solid oxide fuel cells (P-SOFCs) | High protonic conduction at 500–700 °C |
| (La,Sr)BO₃ | Mixed conduction, catalyst | controlled oxidation of hydrocarbons. | Used for SOFC cathodes |
| (B = Mn, Fe, Co) | | Cathode material in SOFCs, membrane | |
| • • • • | | reactors, oxygen separation membranes, | |
| LaAlO ₃ | Host materials for rare-earth luminescent | Substrates for epitaxial film deposition, | |
| YAIO ₃ | ions, | Lasers | |

for stable, sensitive, simple, and selective non-enzymatic glucose sensor such as inorganic perovskite oxides (Jia et al., 2015).

This sensor have perfect electrocatalytic activity toward glucose and H_2O_2 oxidation in alkaline medium due to the occurrence of huge amount of active sites in the modifier.

6.1.3. Neurotransmitters sensor

In the mammalian central nervous system, dopamine (DA) is an essential catecholamine neurotransmitter. The deficiency of this transmitter lead to Parkinson's disease; therefore, its detection is very important but there are very big problem in detection of DA which is the interference of ascorbic acid (AA) and uric acid (UA) with its detection (Jia et al., 2015). Therefore, it is very important to find sensitively and selectively detector to DA even in presence of high concentration of AA and UA.

After electrode modified of SrPdO₃ (CpE/SrPdO₃) it became very good electrochemical DA sensor in living liquids with exclusive long-term constancy and low discovery limit even in the occurrence of high level of AA and UA, it also can sense DA in human urine samples with full selectivity recovery, precision, accuracy, and detection limit (Zhang et al., 2013).

6.2. Solid oxide fuel cells

Fuel cells are used as substitutes to ignition engines due to their possibility to reduce of the environmental pollution. They uses specific type of chemical compound as energy source which transfer to electrical energy like battery. Fuel cells are more acceptable for use due to their effectiveness, spread nature, zero noise pollution, low emissions and its use in future hydrogen fuel economy. There are numerous categories of fuel cells but solid oxide fuel cell are the greatest common samples of fuel cells (El-Ads et al., 2015).

Due to the variances of electrical conductive characteristics of perovskites, they are selected as an active component in SOFC (Wang et al., 2012) because they exhibited its properties of electrical conductivity which is comparable to that of metals with high ionic conductivity, and perfect mixed ionic and electronic conductivity (Atta et al., 2013).

6.3. Catalyst

Perovskite oxides used universally as catalyst in new chemical manufacturing, showing suitable solid-state, surface, and morphological properties (Thirumalairajan et al., 2013). Several perovskites oxides proved to have excellent catalytic activity to different reactions like hydrogen evolution, reduction reactions, and oxygen evolution (Lianghao et al., 2015).

6.4. Solar cells

One of the green source of energy is solar energy because it can be used in replace of the fossil fuels energy. Solar radiation can be transform to electrical energy in a suitable way building numerous uses for solar energy. It can be perfectly changed into electricity using photovoltaic solar cells which built on silicon. The disadvantage of silicon built solar cell is its high price of electricity produced from it, so develop solar cell with low cost is needed (Wang et al., 2012; Li et al., 2016).

Solar cells created on organic/ inorganic solid-state methyl ammonium lead halide hybrid perovskite are in used because it presented better points such 20% lower cost than that of traditional silicon solar cells in addition to the availability of the raw materials (Jin et al., 2013). Perovskite showed outstanding essential properties for photovoltaic applications like suitable band gap, excellent stability, long hole-electron diffusion length, high

absorption coefficient, high carrier mobility & transport, low temperature of processing, charge carriers with small effective mass and easy processing steps (Bao et al., 2015).

7. Conclusion

The unique perovskite structure has the potential to provide a wealth of novel compounds based on A and B site occupancy, which gives rise to a wide range of materials systems with unique properties and wide applications. Several methods were used as synthesizing methods of perovskites compounds such as; Coprecipitation method, Solid-state reactions, Hydrothermal synthesis, Pechini method, Gas phase preparations, Sol-gel method, Low temperature solution combustion method, Microwave synthesis, Roll of PVD methods – laser ablation, MBE, Wet chemical methods. The variety of perovskite compounds synthesizing methods provided materials for many commercial and special technologies in addition to great range of electrical, magnetic, optical and mechanical properties over a wide-ranging temperature.

Depending on Perovskite oxides distinct variety of properties they applied sensors and biosensors for detection of alcohols, hydrogen peroxide pollution, glucose in diabetic patient, and neurotransmitters due to their catalytic routine permanency, high sensitivity to detect minor compounds, selectivity for tested compounds, and inability to be interfere with other compounds.

Also, they showed electronic conductivity, the oxide ions movement through the crystal lattice, differences on the content of the oxygen, chemical stability, photocatalytic, thermoelectric, and dielectric properties. Some perovskites are capable for the improvement of effective anodic catalysts for direct fuel cells showing high catalytic performance.

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