Chapter

Perovskite Structured Materials: Synthesis, Structure, Physical Properties and Applications

Pankaj P. Khirade and Anil V. Raut

Abstract

There is a constant need for newer exceptional materials with better than ever properties to achieve new prerequisites of the future society and progress inventive industrial improvement. The potential to combine these oxides in composite structures to produce multifunctional materials has rekindled interest in perovskites (ABO₃) compounds over the past 10 years. Because of its intriguing characteristics, such as ferroelectricity, piezoelectricity, superconductivity, multiferroicity, photocatalysis, enormous magnetoresistance, dielectric, ionic conduction characteristics, etc., a huge variety of perovskite types have been thoroughly explored. Current applications for perovskite solids include electronics, geophysics, astronomy, nuclear, optics, medicine, the environment, etc. Perovskite compounds have distinctive features that make them suitable for a variety of commercial and technological applications, including capacitors, non-volatile memories, photo-electrochemical cells, catalysts in contemporary chemistry, actuators and sensors, ultrasonic and underwater devices, drug delivery, spintronics devices, tunable microwave devices, and many others. Potential applications for nanoscale perovskites include energy storage, fuel cells, nanomedicine, molecular computing, nanophotonics adjustable resonant devices, catalysts, and sensors. Nanoscale perovskites have intriguing features that are comparable to or better than those of bulk perovskites. This review includes topics such as perovskite structured materials’ chronology, classification, production, crystal structure, special physical properties, and applications.

Keywords: perovskite, ceramics, ferroelectricity, multiferroics, ABO₃

1. Introduction

Perovskites were called for the Russian aristocrat and mineralogist Count Lev Alekseevich Von Perovski (1792–1856), who first discovered the calcium titanium oxide (CaTiO₃) structure in the Ural Mountains of Russia in 1839 [1]. The perovskites materials often contain the generic formula ABX₃, where X is an anion that bonds to both A and B, two cations of quite different sizes [2]. Although X is frequently oxygen, it is also feasible for it to be other big ions such halides, sulphides, or nitrides. Many oxide compounds from a few homologous perovskite series are known, including $A_{n+1}B_{n}O_{3n+1}$ Ruddlesden-Popper, $A_{n}B_{n}O_{3n}$ Dion-Jacobson, $Bi_{2}A_{n-1}B_{n}O_{3n+3}$
Aurivillius series and some others [3–5]. The perovskite structures are exists in different form such as: ABO₃-perovskite (ex: BaTiO₃, CaTiO₃), A₂BO₄-Layered perovskite (ex: Sr₂RuO₄, K₂NiF₄), A₂BB'O₆-Double perovskite (ex: Ba₂TiRuO₆) and A₂A'B₂B'O₉-Triple perovskite (ex: La₂SrCo₂FeO₉), etc. [6–8]. Because of its intriguing range of features, including as superconductivity, insulator-metal transition, ionic conduction characteristics, dielectric properties, and ferroelectricity, perovskite type oxides have been researched extensively [9–12]. One of the most typical solid-state physics structures, perovskite, contains a considerable variety of anions in addition to the majority of the metal ions from the periodic table. Numerous theoretical and experimental studies have focused on perovskite materials, typically ABO₃, over the past few years. These solids are currently assuming a significant role in fields such as electrical ceramics, refractories, geophysics, material science, astrophysics, particle accelerators, fission-fusion reactors, heterogeneous catalysis, environment, etc. [13–22]. In order to maintain their original crystalline structure, perovskite structured oxides can take significant substitutions in either one or both of their cationic sites (i.e., the A and B sites). Through the partial replacement of the cationic site(s) with foreign metal ions, this property enables the chemical customization of the materials, changing their structural, microstructural, electrical, and magnetic properties [23–25]. Perovskite-like compounds and the oxides of the perovskite type have many uses in physics and chemistry. These materials’ physicochemical characteristics are influenced by their pore structure, surface morphology, particle size, exposed lattice plane, lattice defect, and surface morphology [26–29]. Many perovskite-type oxides and perovskite-like oxides have been created and studied so far in order to better understand their physicochemical characteristics. The ideal perovskite is referred to as the cubic perovskite. Due to their straightforward crystal structures and distinctive ferroelectric and dielectric characteristics, this class of materials holds enormous potential for a range of device applications. Perovskites solids, one of the most prevalent and frequently studied minerals, are extensively researched as potential substrate materials [30, 31]. Due to its unique ferroelectric, thermoelectric, pyroelectric, dielectric, and optoelectronic properties, perovskite-structured ceramics (ABO₃, where A and B are two cations) have recently gained popularity on a global scale [32–36]. Perovskite ceramics are used in a variety of exceptional applications, including wireless technology, sensors, actuators, screens, capacitors, random access storage, and adjustable microwave devices [37–44].

2. Perovskite structure

It is known that a perovskite type ABO₃ oxide structure may maintain the stability of almost 90% of the metallic natural elements listed on the periodic table. The crystal perovskite calcium titanate is where the atomic arrangements in this structure were originally discovered (CaTiO₃). The naturally occurring CaTiO₃ species are depicted in Figure 1 (accompanied by Lev Aleksevich von Perovski). The majority of ABO₃-type oxides crystallize in the CaTiO₃ mineral’s (relatively) straightforward form or in a structure quite similar to it. Even though CaTiO₃ was later discovered by Megaw in the United Kingdom, this straightforward cubic form has remained the name perovskite [45]. Subsequently, it was quickly verified with Miyake and Ueda’s work [46]. Perovskites show brittle toughness, a sub-metallic to metallic sheen, colorless streaks, a cube-like structure, and imprecise cleavage. Brown, gray, black, orange, and yellow are among the colors.
The structural formula for perovskite is ABO$_3$, where A and B are cations of varying sizes and O is the anion. Smaller than the B cation is the cation at the A location. According to Figure 2, the A atom has a 12 fold co-ordination number while the B atom has a 6 fold co-ordination number.

Divalent A cations typically reside in the corners of a cube at corner location and are 12 fold coordinated by oxygen anions (0, 0, 0). Tetravalent B cations are located in the body’s core (½, ½, ½) and are found inside that oxygen octahedron. The position (½, ½, 0) of the oxygen atoms in the cubic lattice’s face centre. The structure is typically represented as a three-dimensional network of BO$_6$ octahedra with regular...
corner links. The A atom’s coordination number is 12. A perfect perovskite has a network of shared corner BO6 octahedra with all B-O-B angles at 180 degrees, according to its structure. The proportion of A to B ionic size and the electronic arrangement of the metal ions are two indicators of the structural distortion in perovskite. Perovskite typically exhibits two different structural distortions, one of which is the tilting of the BO6 octahedral and the other of which is the off-centering of the B ion in the BO6 octahedral. The first kind relates to a phase transition that is displacive, and the second type refers to a phase transition that is order-disorder [47, 48]. Tolerance factor ($t'$), introduced by Goldschmidt, can be used to evaluate the prediction criteria for identifying the formability of perovskite structure [49].

$$t' = \frac{(r_A + r_O)}{\sqrt{2 \cdot (r_B + r_O)}}$$

(1)

where $r_A$ and $r_B$ are the ionic radii of the A and B cations, respectively, and $r_O$ is the oxygen anion’s ionic radius (in units). When $t'$ is less than one, the BO$_6$ octahedron tilts; nevertheless, when $t'$ is more than one, the smaller B cation centres off. Off-centering is mostly caused by larger A and smaller B ions, which causes BO$_6$ octahedron to compress. The BO$_6$ octahedron creates a cavity where the B ion tilts more effectively [50]. It has been discovered throughout time that whereas few perovskite-type oxides exhibit the straightforward cubic structure at ambient temperature, many do so at higher temperatures. The ideal perovskite-type structure has a cubic space group Pm3m-Oh [51].

3. Classification of perovskites

Numerous perovskite-based combinations with a variety of physical properties result from the flexibility of the ABO$_3$ perovskite crystalline structure and its capacity to accommodate a broad range of cations with various oxidation states as well as cation or anion vacancies. The two main categories of oxide phases are the ternary ABO$_3$ kind and their solid solutions, and the more modern complicated type compounds (AB',B''$_y$)O$_3$, where B' and B'' are two distinct elements in various oxidation states and $x + y = 1$. On the basis of oxidation states, the ternary oxides can be divided into oxygen and cation deficient species and A$^{1+}$B$^{5+}$O$_3$, A$^{2+}$B$^{4+}$O$_3$, A$^{3+}$B$^{3+}$O$_3$ [52, 53]. The flowchart below Figure 3 displays the comprehensive classification.

A(B$_{x}$B'$_{y}$')O$_3$ is a complex perovskite type compound that can be separated into A (B'$_{0.67}$B''$_{0.33}$)O$_3$ compounds that contain twice as much a lower valence state element as a higher valence state element, those that have A(B'$_{0.33}$B''$_{0.67}$)O$_3$, which has twice as much of the higher valence state element as the lower valence state element. Those with A(B'$_{0.5}$B''$_{0.5}$)O$_3$, those with equal levels of the two B components A(B'$_{x}$B''$_{y}$')O$_3$ and oxygen-deficient phases. The A and B cations’ electron orbitals are typically near to 2$^+$ and 4$^+$, correspondingly, but in a few unique situations, they may be 3$^+$ and 3$^+$ if the B$^{3+}$ cation has a six coordination. The oxygen anion array may be bent or displaced as a result of the valence variation at the A cation site, which will buckle the (AO3)$^{4-}$ layers. The octahedra with B cations at their centres may become distorted as a result of this buckling. Due to their multiple valencies or unique 3d and 4d electron configurations, transition metal elements are good candidates to fill the B cation position because they have the adaptability needed to withstand this impact. This explains why transition metal oxides typically exhibit exceptional physical properties and feature perovskite-like structures. The oxygen and cation deficient phases will be viewed as
having a significant amount of vacancies rather than being just out of stoichiometry. Many of them differ from the complex perovskite compounds, which contain various elements in various valence states, in that they contain B ions of one element in two valence states [54, 55].

4. Synthesis of perovskites

When production of superior ceramic powders for advanced technology the ceramics industries are developing into one of the most important and quickly
expanding sectors. Particularly, there will be a lot of interest in the creation of fine ceramic powders with exceptional and uncommon qualities. Regarding the structural and physico-chemical characteristics of perovskite structured materials, the synthesis processes are crucial. A crucial duty is sample synthesis, which can be accomplished via a variety of synthesis approaches [56]. Perovskites can be prepared in various forms like nanocrystalline [57], bulk [58], thin films [32], nanowires [59], nanotubes [60], nanocubes [61], nanorods [62] etc. forms depending on its applications using particular bottom-up and top down approach. There are several methods to synthesize perovskite materials in different forms such as chemical co-precipitation [63], microemulsion [64], hydrothermal [65], solvothermal [66], microwave irradiation [67], spray-pyrolysis [68], chemical vapor deposition [69] etc. The sol-gel auto combustion approach for bulk and nanoparticles of the BaTiO$_3$ solid is highlighted here with a brief explanation of the solid-state reaction.

4.1 Solid state reaction method

The majority of prior research on perovskite materials concentrated on their solid-state reaction-produced structure and physical characteristics. The most popular technique for creating polycrystalline bulk solids from a variety of solid starting materials is the solid-state reaction approach, sometimes referred to as the ceramic method. The solid state reaction pathway offers a wide variety of raw materials, including oxides, carbonates, etc. At room temperature, solids do not react with one another; therefore, it is required to heat them to much higher temperatures, typically between 800 and 2000°C, for the reaction to take place at an acceptable rate. Consequently, in this strategy, both the thermodynamic and kinetic elements are crucial [70]. Precursor materials BaCO$_3$ and TiO$_2$ were combined to create bulk BaTiO$_3$, and the mixture was then pulverized with a mortar and pestle to reduce the size of the particle sizes and increase the surface area exposed to the reaction. The crushed powder was calcined in furnace over 900°C to form the necessary product. Different wet chemical techniques can be used to overcome the limitations of the traditional solid state reaction approach, including high sintering temperature, secondary phase formation, poor ingredient dispersion, high porosity, and big particle size [71]. Due to its higher surface-to-volume ratio and quantum confinement effects, nanomaterials have different properties than those of bulk materials [72]. It is a widely acknowledged fact that the properties of a bulk material radically alter as it gets closer to the nanoscale. These characteristics are related to the size, shape, and distribution of the particles inside the materials, which in turn are dependent upon the synthesis process.

4.2 Sol-gel auto combustion method

Another name for the sol-gel auto combustion process is low-temperature self-combustion, commonly known as auto-ignition, self-propagation, nitrate-citrate combustion, gel-thermal breakdown technique, etc. [73]. This method uses a sol-gel procedure to create a gel out of an aqueous solution of the necessary metal salts (often nitrates or acetates) and organic fuel. The gel is then ignited to cause combustion, producing a fluffy, voluminous end product with a sizable surface area. Fuel is utilized in this procedure as a complexant to create a homogenous precursor called xerogel [74]. In comparison towards other synthesis techniques, a sol-gel auto combustion approach has unquestionable advantages since it can precisely manage the composition, purity, least particle aggregation, homogeneity at the microscopic scale, and
sintering temperature [75]. Here, a straightforward procedure for producing nanocrystalline BaTiO$_3$ material is described. Selecting the proper complexant additives is crucial for the production of homogeneous phases. Metal particles of varying sizes can be successfully chelated by complexant agents or fuel, which helps to maintain the specific precipitation needed to maintain compositional homogeneity among the constituents. The complexant substances act as reductants and are oxidized by nitrate ions to produce fuel. According to a literature review, many types of complexant agents are utilized to create perovskite materials. Most commonly used complexants are citric acid (C$_6$H$_8$O$_7$), glycine (NH$_2$CH$_2$COOH), urea (CO(NH$_2$)$_2$), ethylene glycol (CH$_2$OH)$_2$, dextrose (C$_6$H$_12$O$_6$), acetic acid (CH$_3$COOH), ascorbic acid (C$_6$H$_8$O$_6$), propionic acid (CH$_3$CH$_2$COOH) etc. [76]. Here, tetra butyl titanate (Ti(OC$_4$H$_9$)$_4$) or titanium isopropoxide Ti[OCH(CH$_3$)$_2$]$_4$ can be chosen as a precursor (for Ti$^{4+}$ ions) due to the fact that it is a transition metal alkoxide. It is very reactive because it contains strongly electronegative groups that keep the metal in the highest oxidation state and enable nucleophilic attack on the metal. These alkoxide precursors are highly electrophilic, making them less resistant to condensation, hydrolysis, and other nucleophilic processes. Additionally, the group R from Ti(OR)$_4$ influences the gel’s shape (size and surface area of the crystallites) and crystallization behavior. Controlling the condensation path and polymer development requires chemical modification of the transition metal alkoxide with chelating ligands. Tetra butyl titanate was chelated with ethanol (1:2) to produce a highly condensed product and to aid in the gelification process. A unidimensional polymer is produced when too much water is introduced to (Ti(OC$_4$H$_9$)$_4$)-ethanol, which causes the O-R ligands to be hydrolyzed preferentially [77]. The metal nitrate to citric acid molar concentration was taken to be 1:5 in accordance with the rules of propellant chemistry, which take into account the oxidizing and reducing valencies of various components. The total valence of the precursors was used for this Ba(NO$_3$)$_2$ = −10, C$_6$H$_8$O$_7$ = +18 and Ti(OC$_4$H$_9$)$_4$ = +96. Tetra butyl titanate solution was initially added to a citric acid aqueous solution with a pH of 8, which was then brought to the desired level by adding the necessary amount of ammonia. A yellowish translucent liquid that is designated as solution “A” was produced after being agitated at 80°C for 1 hour. Inorganic compounds (in this case, barium nitrate) were simultaneously dissolved in distilled water while being continuously stirred; the resulting solution, designated as solution “B,” is the result. Then, mixtures of solutions “A” and “B” were added. Ammonia was used to bring the pH level to 7 and maintain it there until a translucent liquid was obtained. The solution’s viscosity progressively rose after 3 hours of nonstop stirring, after which a stable translucent sol formed. The creation of the gel is started by continuous heating to 110°C. Viscous gel becomes dry gel when heated and constantly stirred. It was discovered that the nitrate-citrate gel’s combustion process was autocatalytic, and experimental results revealed that the dried gel made of metal nitrates and citric acid exhibited self-propagating combustion behavior. The entire combustion process was completed in a matter of minutes. To produce the nanocrystalline powders, the resulting powders were dried, crushed, and annealed at 900°C for 5 hours in a muffle furnace. Figure 4 shows the process for making BaTiO$_3$ nanoceramics using the sol-gel method.

5. Unique properties of perovskites

The ceramic materials with the general chemical formula ABO$_3$ made of perovskite are utilized as high-value materials in a variety of engineering and technological
applications. Because of the non-stoichiometry of the cations and/or anions, the distortion of the cation configuration, and the mixed valence and valence mixture electronic structure, perovskite-type structures have functional features. Furthermore, it is known that the majority of the naturally occurring metallic elements are stable in perovskite-type oxide structures, and the ability to synthesize multicomponent perovskites by partially substituting cations in positions A and B results in a variety of complicated kinds. These traits are what give perovskites their unique qualities. These include ferroelectric, thermoelectric, multiferroic,
superconductive, dielectric, optical, and many more unique properties. A few of them are described in depth here [78–80].

5.1 Dielectric properties

Materials that allow electro-static fields to last a long time are known as dielectric or electrical insulating materials [81]. The basic electrical properties of conductive materials and dielectric materials sharply diverge because the dielectric materials offer a very high resistance to the channel of electric current under the influence of the applied direct-current voltage. Capacitors frequently have layers of these materials added to them to improve performance; the term “dielectric” specifically refers to this use [82]. Ferromagnetic or high dielectric permittivity materials are crucial for the production of electroceramics in engineering and electronics. BaTiO₃ and KNbO₃ are two examples of perovskites that have undergone substantial research in the past [35, 83]. The ratio of a substance’s permittivity to the permittivity of empty space is known as the dielectric constant. A significant dielectric constant (ε), which is a highly nonlinear and anisotropic incident, is based on the collective polar deflections of the metal ions with respect to the oxygen sublattice [84]. A soft-mode model typically describes the phase shift that results in ferroelectricity [85]. Many variety of careers have been taken from the structurally straightforward BaTiO₃ by the solid coordination compound Pb(Zr,Ti)O₃ to various unique families of materials in order to adjust the dielectric and mechanical properties [86]. These approaches specifically account for the fact the perovskites’ adaptability to chemical alteration and docility [87]. The relaxor ferroelectric is one of them. It is undoubtedly based on a multi-element substituted lead titanate (PbTiO₃) with the chemical formula A(B′B″)O₃ with random metal cation occupants at the A and B sites with various valence states and ionic radii [88, 89]. Large dielectric constants, a clear frequency dispersion, and temperature-dependent dielectric constant variations are all characteristics of relaxor ferroelectrics. For temperatures above the glass transition, these effects result from slow relaxation processes [90]. The effects are based on electrical inhomogeneities and the presence of polar nano-regions, and their length scales for changing composition and spontaneous polarization are 2–5 nm. The lattice component of the response is thought to constitute a local softening of the transverse-optical phonon branch that prevents long-wavelength (q = 0) phonon propagation. It is remarkable to notice that for such small length scales, the basic limit, the superpara-electric state, has not yet been attained [91]. PZT and PMN are two general examples of relaxor ferroelectrics [92]. Two common examples of relaxor ferroelectrics are PZT and PMN (e.g. SrTiO₃) [93]. Perovskites, such as BaTiO₃, are one of the potential possibilities for usage in dynamic random access memory (DRAM) and tunable microwave devices due to their high dielectric constant and low dielectric loss [94, 95].

5.2 Superconductivity

When cooled below a specific critical temperature, certain materials exhibit the phenomena of superconductivity, which results in exactly zero electrical resistance and the expulsion of magnetic flux fields [96]. A wide family of materials with a variety of crucial physical characteristics is known as oxide perovskites. Notably, this form of perovskite structure offers a superb structural foundation for the presence of
superconductivity. The most well-known examples of superconducting perovskites are high $T_c$ copper oxides, although there are other others as well [97]. Many superconducting materials have historically come from intermetallic compounds, however perovskite oxides have recently overshadowed their existence. Sweedler et al. looked at the tungsten bronzes’ superconductivity [98]. Bronzes made of cesium, sodium, potassium, rubidium, and tungsten were discovered to be superconductors. Three samples of decreased strontium titanate were examined by Schooley and colleagues to measure superconducting transitions [99]. The reduced crystals were made by heating for a lengthy time in a vacuum between $10^{-5}$ and $10^{-7}$ mm Hg. The transitions happened at respective temperatures of 0.25 K and 0.28 K. Additionally, superconductivity has been discovered in the systems’ decreased phases $\text{Ba}_{x}\text{Sr}_{1-x}\text{TiO}_3$ and $\text{Ca}_y\text{Sr}_{1-y}\text{TiO}_3$ when $x \leq 0.1$ and $y \leq 0.3$ [100].

Superconductors classified as “Type 2″ are made of metallic compounds and alloys (except for the elements vanadium, technetium and niobium). This Type 2 group includes the recently found superconducting “perovskites” metal-oxide ceramics, which typically have a ratio of 2 metal atoms to every 3 oxygen atoms. They outperform Type 1 superconductors in terms of transition temperature $T_c$ by a mechanism that is yet not fully understood [101]. The discovery that $\text{Ba(Pb,Bi)O}_3$ had a $T_c$ of 13 K in 1973 by a DuPont research team led to the development of the first of the oxide superconductors [102].

5.3 Ferroelectricity

“You may say anything you like but, we all are made up of ferroelectrics”.  
(B. T. Matthias).

Ferroelectricity is a phenomena in which the introduction of an external electric field induces a spontaneous electric polarization in some materials [103]. Various crystals, including quartz, tourmaline, and Rochelle salt, exhibit piezoelectricity, which was discovered by brothers Pierre and Paul-Jacques Curie in 1880 [104, 105]. This discovery inspired subsequent research in the topic of piezoelectrics, most notably Erwin Schrodinger’s work [106, 107]. Erwin Schrodinger originally used “ferroelektrisch” or “ferroelectricity” in 1912 [108]. Joseph Valasek is credited with finding ferroelectricity for his systematic investigation of the magnetic characteristics of ferromagnetic and the dielectric properties of rochelle salt, which he presented at the American Physical Society’s annual conference in Washington on April 23, 1920 [106]. The early 1940s saw the discovery of ferroelectricity in materials based on perovskite, such as barium titanate ($\text{BaTiO}_3$), which was a significant advance in the field of ferroelectric research [109, 110]. There is a lot of interest in various forms of ferroelectrics as a result of the finding of ferroelectricity in $\text{BaTiO}_3$. This discovery opened up new application possibilities for ferroelectric materials [105, 111]. Ven’skev and Zhdanov identified the perovskite family’s distribution of ferroelectrics (FE) and antiferroelectrics (AFE) [112]. The FEs cover the entire perovskite range $0.78 \leq t' \leq 1.05$. The AFEs are found to have a restricted distribution ($0.78 \leq t' \leq 1.0$). In addition to classifying ferroic behavior in perovskites using the tolerance factor ($t'$), Halliyal and Shrout discovered that graphing $t$ against the average electronegativity as indicated by [112];

$$\chi = (\chi_{AO} + \chi_{BO})/2$$

(2)
where the electronegativity differences between the A and B cations and oxygen are denoted by $\chi_{AO}$ and $\chi_{BO}$, respectively. The endurance of the crystalline phase for a variety of simple and complicated perovskites was discovered. Perovskite compounds with low $t'$ extended to develop pyrochlore phase(s), and the perovskite phase was stabilized by solid solutions in which $t'$ was raised [113]. The dielectric constant of ferroelectric materials is about two orders of magnitude more than that of regular dielectric. A well-known ferroelectric substance with a relative dielectric constant of above 2000 is BaTiO$_3$. Ferroelectric materials must include permanent electric dipoles; one of the most common ferroelectrics, barium titanate, is explained for its creation [114]. The spontaneous polarization is a consequence of the positioning of the Ba$^{2+}$, Ti$^{4+}$, and O$^{2-}$ ions within the unit cell, as represented in Figure 5a.

The O$^{2-}$ anions are at the face centres, the Ti$^{4+}$ ion is in the octahedral void at the body centre, and the Ba$^{2+}$ ions are in the body corners. Only one of the four octahedral voids in the unit cell is filled, which matches the chemical formula of one titanium for every four species of the other kinds: one barium plus three oxygen. Barium titanate is a cubic crystal with the ion positions mentioned above 120°C [115]. The positive and negative charge centres coincide in this instance, and a spontaneous dipole moment is absent. The Ti$^{4+}$ ion shifts to one side of the body centre if the crystal is cooled below the Curie temperature of 120°C, as indicated by the dotted line in Figure 5's front view (b). A displacement of the nearby oxygen anions also occurs.

At normal temperature, the crystal changes from its cubic phase to its tetragonal phase. The tetragonal cell’s $c/a$ ratio is almost 1.012. Local dipoles are formed all around the crystal as a result of the positive and negative charge centres no longer lining up. A significant amount of polarization occurs in the solid as a result of the alignment of the dipoles of nearby unit cells. Even when the dipoles of nearby unit cells are aligned, a BaTiO$_3$ crystal typically displays no net polarization at ambient temperature in the absence of an external field. This can be understood by visualizing the behavior of ferroelectric domains in a manner similar to that of ferromagnetic domains. When an electric field is applied, the domains have a tendency to line up in the field’s direction, and we notice all the hysteresis loop phenomena, including domain rotation and domain growth. A ferroelectric hysteresis loop is shown in

Figure 5.
BaTiO$_3$ crystal unit cell in (a), with the Ti$^{4+}$ ion and O$^{2-}$ ions migrating out from the centre as indicated by the arrows in (b).
For the creation of sensors, capacitors, memory devices, etc., ferroelectric properties are exploited. Ferroelectric materials have a non-linear feature that tunable capacitors take advantage of to tune the capacitance. Two electrodes and a layer of ferroelectric material sandwich each other in the ferroelectric capacitor. Comparatively speaking to non-tunable dielectric capacitors, ferroelectric capacitors are both tunable and very compact in size. Ferroelectric materials’ hysteresis during spontaneous polarization can be used to create ferroelectric RAM and RFID cards. Input devices in ultrasonic imagers, infrared cameras, fire sensors, motion detectors, etc., use ferroelectric material.

### 5.4 Piezoelectricity

The capacity of some materials to produce an electric charge in response to applied mechanical stress is known as piezoelectricity. The Curie brothers, Pierre and Jacques, discovered the piezoelectric effect in 1880 [118]. They discovered that certain crystals became electrically polarized when subjected to mechanical strain, and the amount of polarization was proportional to the applied strain. The Curies also found that when subjected to an electric field, the same materials distorted. The inverse piezoelectric effect has been coined to describe this [119]. Figure 7a and b show, respectively, the piezoelectric effect and the inverse piezoelectric effect.

By interacting with one another, electric dipoles spontaneously align in ferroelectric materials, whereas in piezoelectric materials, an additional force is needed. In light of this, all ferroelectrics are also piezoelectrics, but not vice versa [120]. The piezoelectric ceramics, of which PZT is an example, are a significant group of piezoelectric materials in addition to the crystals already described [121]. These are perovskite-based polycrystalline ferroelectric materials, which have tetragonal/rhombohedral...
crystal structures that resemble cubic shapes. They possess the common formula $A^{2+}B^{4+}O_{2}^{-3}$, where $A$ stands for a big divalent metal ion, like lead or barium, and $B$ stands for a tetravalent metal ion, like titanium or zirconium.

5.4.1 Mathematical modeling

Piezoelectricity is a result of combining Hook’s law with the electrical behavior of materials [122]:

\[ D = \varepsilon E \]  \hspace{1cm} (3)

\[ S = sT \]  \hspace{1cm} (4)

where, $D$: electric displacement, $\varepsilon$: permittivity, $E$: electric field strength, $S$: strain, $s$: compliance, and $T$: stress.

The coupled strain-voltage equation:

\[ S = sTE + dT \]  \hspace{1cm} (5)

\[ D = \varepsilon TE + dE \]  \hspace{1cm} (6)

\[ D_{ij,k} = dS_{ij} \]  \hspace{1cm} (7)

\[ D_{ij,k} = \frac{dS_{ij}}{dE_{k}} \]  \hspace{1cm} (8) piezoelectric coefficient

Natural materials including quartz, cane sugar, collagen, topaz, dna, rochelle salt, wood, and tendon are examples of piezoelectric materials. Man-made crystals and ceramics include langasite, gallium orthophosphate (GaPO₄), and quartz analogous crystals (La₃Ga₅SiO₁₄), quartz analogic crystal, barium titanate, lead zirconate titanate etc. Acousto-optic modulators, valves, high voltage and power sources, cigarette lighters, energy harvesting, AC voltage multipliers, piezoelectric motors, actuators, loudspeakers, pressure sensors, force sensors, strain gauges, microphones, pick-ups, actuators, and many other applications use piezoelectric materials.
5.5 Magneto-electronic correlations

In perovskites containing transition metal ions with open 3d electron shells, magnetism or different orbital (electronic) ordering phenomena are seen. When compared to other electronic states, these 3d states have a larger ratio of the Coulomb repulsion energy $U_d$ to the bandwidth $W$, which gives them a more localized character and a propensity for insulating states or metal-insulator transitions [123]. Due to the overlap of the different wave functions, these electrons hop and super-exchange via oxygen sites. Thus, non-stoichiometry and the [BO6] octahedra’s tilt or distortion have a significant impact on the characteristics and phase diagrams of a perovskite. Additional factors include charge doping, charge/orbital inhomogeneous states that cause enormous response, such as to external magnetic fields, and order/disorder processes of the orbital part of the 3D wave function [23]. But before taking into account such effects, the electronic structure, the number of 3d electrons, the Hund’s Rule coupling, the crystalline electric field or Jahn-Teller splitting of the 3d electronic configuration a hierarchy of energies that describes the properties of the system.

5.6 Multiferroicity

“Materials should exist, which can be polarized by a magnetic field and magnetized via an electric field.” P. Curie. A remarkable class of materials displaying simultaneous ferromagnetic, ferroelectric, and ferroelastic ordering is represented by multiferroics. H. Schmid coined the term “multiferroic” in 1994 [124]. Multiferroic materials with the corresponding properties are shown in Figure 8. These materials are unique in that they have the capacity to simultaneously use both their magnetization and polarization states, a huge potential that would make them excellent candidates for next-generation sensors and memory technology [125, 126]. Numerous multiferroics, such as rare-earth manganites and ferrites, are transition metal oxides with perovskite crystal structure (e.g. HoMn$_2$O$_5$, TbMnO$_3$, LuFe$_2$O$_4$) [127, 128]. Ba$_2$CoGe$_2$O$_7$, Ca$_2$CoSi$_2$O$_7$, TbFe$_3$(BO$_3$)$_4$, CoCr$_2$O$_4$, FeCr$_2$O$_4$, MnCr$_2$O$_4$, NdFe$_3$(BO$_3$)$_4$ are those substances that exhibit multiferroicity even at ambient temperature [129–132]. Bismuth ferrite (BiFeO$_3$), a rhombohedrally distorted

Figure 8.
Multiferroic materials.
Perovskite, is one of the many multiferroics that have been studied, and it is receiving constant attention because it exhibits both ferroelectric order and anti-ferromagnetic order over a wide temperature range that is significantly above room temperature [133]. The majority of ferromagnetic materials are typically metals, therefore a ferroelectric material must be an insulator. As a result, the simultaneous occurrence of ferroelectric and ferromagnetic ordering is constrained by the lack of ferromagnetic insulators. Multiferroics are still uncommon even when antiferromagnetic systems are taken into account. A structural deformation from the high symmetry phase, which removes the centre of inversion and enables an electric polarization as seen in Figure 9, is the traditional prerequisite for ferroelectricity. Ferroelectricity and ferromagnetism exhibit synchronous time and spatial inversion breaking in Figure 9. Unpaired d electrons are necessary for any type of magnetic ordering, however ferroelectric materials like typical perovskite oxides lack this property (ABO₃) have a d⁰ configuration on the small B cation. The tendency for the tiny cation to generate a distortion that removes the centre of symmetry is significantly suppressed if the d shell is only partially populated. With some unpaired electrons in the d orbitals, magnetoelectric multiferroic materials should therefore exhibit some deformation in their crystal structure. Recently, it was discovered that magnetic spin ordering can create ferroelectricity even in the absence of any structural distortion. As a result, there are now a lot more ferroic materials that could be used [134]. Experimental and theoretical research both point to a new era in the attainability of multiferroicity in transition metals doped BaTiO₃ [135]. Extrinsic and intrinsic dopants like excess oxygen vacancies and transition metal cations can be added to these materials to improve their chemical and physical properties [136].

The electrical or magnetic characteristics of perovskites with transition metal ions (TM) doped on the B site are incredibly diverse and intriguing. This variety is more closely linked to the intricate role that transition metal ions play in certain coordinations with oxygen or halides than it is to the chemical flexibility of these compounds [137]. Although unfilled 3d electron shells of the TM are typically associated with magnetism and electronic correlations, filled 3d electron shells are associated with strong dielectric characteristics. Due to the limited number of low-symmetry magnetic point groups that permit spontaneous polarization, multiferroicity, the coexistence of spontaneous ferroelectric and ferromagnetic moments, is a rare phenomenon [138]. One of two categories can be used to group all multiferroic materials. Multiferroics of type I and type II. At high temperatures, Type I go through a structural, nonpolar-to-polar phase transition that, in most cases, involves the breaking of inversion symmetry and results in ferroelectricity. At lower temperatures, the emergence of magnetic order takes place below a different phase transition. The main order

![Figure 9. The prerequisites for ferromagnetism and ferroelectricity (polarization) (unpaired electron spin motion).](http://dx.doi.org/10.5772/intechopen.106252)
Recent Advances in Multifunctional Perovskite Materials

parameter for type II is the staggered antiferromagnetic) magnetization. Below a certain temperature, magnetic ordering transforms the symmetry group from a non-polar parent phase to a polar magnetic phase. This results in inappropriate ferroelectricity. Additionally, magneto-structural coupling to the crystal structure creates an electrically polar state. However, polar non-centrosymmetric magnetic structures typically originate from the complicated magnetic ordering of geometrically frustrated states or from competing interactions in this situation, where the magnetic and ferroelectric order parameters are intimately related [139].

5.7 Optical properties

Perovskites have emerged as a revolutionary class of materials having excellent optical and photoluminescence properties. W.J. Merz studied the optical properties of single domain crystals of BaTiO₃ at various temperatures [140]. The crystal’s refractive index was almost constant at ~2.4 between 20 and 90 degrees Celsius and peaked at ~2.46 at 120 degrees. BaTiO₃’s index of refraction was also measured by W.N. Lawless and R.C. De Vries at 5893 in the temperature range of 20–105°C; above Curie point, the index increased ~1.3 percent to 2.398 and stayed constant to 160°C [141]. It was discovered that the single BaTiO₃ crystal, which is 0.25 mm thick, transmits between 0.5 μ and 6 μ. A weak absorption band was identified near 8, and complete absorption was found for wavelengths longer than 11 μ. Noland reported on the optical characteristics of single crystals of strontium titanate created during flame fusion [142]. The wavelength range where the optical coefficient was obtained was 0.20–17 μ. From 0.55 μ to 5 μ, a transmission of more than 70% was seen. These crystals have an index of refraction of 2.407 at 5893 Å, a dielectric constant of 310, and a loss tangent of 0.00025. Linz and Herrington reported the optical density of CaTiO₃ [143]. With the exception of the absorptions being shifted to shorter wavelengths, the absorption properties are remarkably comparable to those of SrTiO₃ crystals. High temperature infrared windows have been considered for BaTiO₃ and SrTiO₃. SrTiO₃ is regarded as a superior material for infrared detectors that are optically submerged. The detector-lens combinations are frequently chilled to liquid N₂ and solid CO₂ temperatures to boost sensitivity. Geusic et al. evaluated the electro-optic characteristics of K(Ta₀.₆₅Nb₀.₃₅)O₃, BaTiO₃ and SrTiO₃ in the paraelectric phase [144]. When the distortions of the optical indicatrix are described in terms of the induced polarization, the electro-optic coefficients of these perovskites are almost constant with temperature and from material to material. These experiments also demonstrated the K(Ta₀.₆₅Nb₀.₃₅)O₃’s strong electro-optic action at ambient temperature. There has been a lot of interest in materials that can be applied using lasers in recent years. Perovskite laser host materials are widely used. The most often used ion for insertion into somewhat large crystallographic locations seems to be Nd³⁺. However, compensatory ions are necessary in these substitutions, barring the usage of LaF₃ as a host. Without compensating ions, divalent Tm²⁺ and Dy²⁺ can be substituted in CaF₂, but they are very unstable. Cr³⁺ turned shown to be the best replacement for Al³⁺ at its crystallographic positions. Recent studies have increasingly concentrated on the luminous characteristics of rare earth ion doped perovskite-type oxides. Oxygen phosphors of the perovskite type are exceedingly stable and can consistently function in a variety of conditions. [145–147]. Additionally, Perovskite-type oxide phosphors have been discovered to be a likely contender in field emission display (FED) and plasma.
display panel (PDP) systems because they are sufficiently conductive to release electric charges on the phosphor particle surfaces [148]. Many perovskite-type oxide phosphors, such as $A^{2+}B^{4+}O_3$ ($A =$ Ca, Sr, Ba; $B =$ Ti, Zr, Si, Hf, etc.) are therefore activated by rare earth ions, such as $\text{Sm}^{3+}$, $\text{Tm}^{3+}$, $\text{Pr}^{3+}$, $\text{Eu}^{3+}$, $\text{Tb}^{3+}$ and so forth [149–151] have been made, and their luminous characteristics have also been extensive examination. There aren’t many research on photoluminescence (PL) in zirconates, particularly ones with visible emission regions [152]. Phosphors of rare earth ions doped perovskite type oxides, such as $\text{SrHfO}_3$:Ce [153] and $\text{CaTiO}_3$:Pr [154] X-ray phosphors could be used in many displays, hence current study has concentrated on their luminous qualities. $\text{Eu}^{3+}$ is an effective activator ion that emits red or red-orange light in a variety of hosts, including borates [155], niobates [156] and molybdates [157]. Host $\text{BaZrO}_3$ is now recognized as a readily available, inexpensive, and environmentally benign photoluminescence (PL) material that produces light in the visible spectrum [158]. This material is promising because of its PL feature, which makes it useful for applications including scintillators, plasma displays, solid state lightning, green photocatalysts, and field emission displays [159–161].

5.8 Colossal magnetoresistance (CMR)

Some materials have a feature called colossal magnetoresistance (CMR) that allows them to drastically alter their electrical resistance when a magnetic field is present (mostly manganese-based perovskite oxides) [162]. CMR was first identified in mixed-valence perovskite manganites in the 1950s by G. H. Jonker and J. H. van Santen [163]. Due to their rich fundamental physics and significant potential for use in spintronics devices, the discovery of the colossal magnetoresistance (CMR) influence in divalent alkaline-earth ion dopant perovskite manganites $\text{Re}_{1-x}\text{A}_{x}\text{MnO}_3$, where Re is a trivalent rare-earth (La, Pr, Sm, etc.), has generated a great deal of interest [164–167]. Different magnetic phases, including insulating antiferromagnetic phases with multiple orbital orders and a ferromagnetic, metallic, orbitally disordered phase, are detected depending on the orbital occupancy of the manganese ions and the related orbital order. Because of the close coupling between spins and orbitals in these compounds, both degrees of freedom have ordering temperatures that are similar in magnitude. In a three-dimensional lattice, the primary spin exchange pathways pass over almost 180 TM-O-TM limits (TM-transition metal). But merely taking into account spins, low dimensionality, magnetic frustration, and quantum processes can also result in some incredibly strange phase diagrams, even ones without magnetic long range order [168]. In fact, in frustrated lattices, quantum fluctuations or a second order energy scale can frequently lift the degeneracy of the magnetic ground state [169, 170]. The nature of CMR manganites, which are strongly correlated electron systems with interactions between the lattice, spin, charge, and orbital degrees of freedom, including the double exchange interaction, Jahn-Teller effect, electronic phase separation, charge ordering, etc., is generally thought to be the root cause of the CMR effect. This theory has been extensively discussed in some review papers [171–175].

6. Applications of perovskites

Calcium titanate ($\text{CaTiO}_3$)-like perovskite materials offer fascinating and exceptional physical features that have been thoroughly investigated for use in
both theoretical modeling and real-world applications. Due to their extremely stable structure, abundance of compounds, diversity of characteristics, and several useful applications, inorganic perovskite-type oxides are fascinating nanomaterials with a wide range of uses. Current applications for these solids include electronics, geophysics, astronomy, nuclear, optics, medicine, the environment, etc. [176].

Perovskites are useful for many different applications depending on the aforementioned distinctive properties, including thin film capacitors, non-volatile memories, photoelectrochemical cells, recording apps, read heads in hard discs, spintronics devices, laser applications, for windows to block high temperature infrared rays, high temperature heating applications (thermal barrier coatings), frequency filters for wireless technology, non-volatile memorabilia, and spintronics devices. Table 1 lists additional significant uses for various perovskite-structured materials, along with the corresponding characteristics.

<table>
<thead>
<tr>
<th>Reference compound</th>
<th>Properties</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO₃</td>
<td>Dielectric ferroelectric</td>
<td>Multilayer ceramic capacitors (MLCCs), sensor, PTCR resistors, embedded capacitance [177–179]</td>
</tr>
<tr>
<td>PbTiO₃</td>
<td>Pyroelectric piezoelectric</td>
<td>Transducer, pyrodetector, under water devices [180, 181]</td>
</tr>
<tr>
<td>(BaSr)TiO₃</td>
<td>Non-linear dielectric properties, pyroelectric</td>
<td>Tunable microwave devices, pyrodetector [182]</td>
</tr>
<tr>
<td>Pb(ZrTi)O₃</td>
<td>Dielectric, pyroelectric, piezoelectric, electro-optic</td>
<td>Nonvolatile memory, ferroelectric memories (FERAMs), surface wave acoustic devices, substrate wave guide devices [183, 184]</td>
</tr>
<tr>
<td>Bi₄Ti₅O₁₂, high Tₓ cuprate compounds</td>
<td>Ferroelectric with high Curie temperature superconductivity</td>
<td>High-temperature actuators, FeRAMs [185, 186]</td>
</tr>
<tr>
<td>BaCeO₃, BaZrO₃</td>
<td>Proton conduction</td>
<td>Electrolyte in protonic solid oxide fuel cells (P-SOFCs) [187]</td>
</tr>
<tr>
<td>LaNiO₃</td>
<td>Chemical</td>
<td>Catalysts [188]</td>
</tr>
<tr>
<td>(La,Sr)MnO₃</td>
<td>Colossal magnetoresistance</td>
<td>Spintronics devices [189]</td>
</tr>
<tr>
<td>Pb(Mg₁/₃Nb₂/₃)O₃</td>
<td>Dielectric</td>
<td>Memory device, capacitor [190]</td>
</tr>
<tr>
<td>K(TaMn)O₃</td>
<td>Pyroelectric, electro-optic</td>
<td>Waveguide device, frequency doubler [191]</td>
</tr>
<tr>
<td>BiFeO₃</td>
<td>Magnetoelectric coupling, high Curie temperature</td>
<td>Magnetic field detectors, memories [192, 193]</td>
</tr>
<tr>
<td>(La,Sr)BO₃ (B = Mn, Fe, Co)</td>
<td>Mixed conduction, catalyst</td>
<td>Cathode material in SOFCs, oxygen separation membranes, membrane reactors, controlled oxidation of hydrocarbons [194, 195]</td>
</tr>
<tr>
<td>(KₓNaₓ)₂NbO₆, NaₓBi₂O₅TiO₃</td>
<td>Ferroelectricity, piezoelectricity</td>
<td>Lead-free piezoceramics [196, 197]</td>
</tr>
<tr>
<td>LaAlO₃, YAlO₃</td>
<td>Host materials for rare-earth luminescent ions,</td>
<td>Lasers Substrates for epitaxial film deposition [198, 199]</td>
</tr>
</tbody>
</table>

Table 1. Applications of perovskites along with respective properties.
7. Conclusions

This chapter primarily addresses the fundamental concepts of perovskites, their structure, classification of perovskites, their synthesis, their distinctive features, and their applications. Because of its many unique properties, including enormous magnetoresistance, multiferroics, superconductivity, etc., perovskite structured materials have received a great deal of research attention. Perovskites have unique and unusual physical properties that have been extensively studied for both real-world use and theoretical research. Applications for photonic and optoelectronic devices, effective solar cells, fuel cells, spintronics, electrical machines, random-access memory, electrochemical double layer capacitors, and other novel device concepts are just a few of the many novel device concepts that have been made possible by perovskites in the field of materials science.

Acknowledgements

The author thanks Dr. K.M. Jadhav, Senior Professor in the Department of Physics at the Dr. Babasaheb Ambedkar Marathwada University in Aurangabad, India, for a lively discussion and insightful advice.

Conflict of interest

The authors declare no conflict of interest.

Author details

Pankaj P. Khirade¹* and Anil V. Raut²

1 Department of Physics, Shri Shivaji Science College, Amravati, India

2 Department of Physics, Vivekanand Arts, Sardar Dalipsingh Commerce, and Science College, Aurangabad, India

*Address all correspondence to: pankajkhirade@gmail.com; nano9993@gmail.com

IntechOpen

© 2022 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
References


[28] Ghazanfari MR, Amini R, Shams SF, Alizadeh M, Ardakani HA. Effect of mechanical alloying synthesis process on the dielectric properties of (Bi 0.5 Na 0.5) 0.94 Ba 0.06 TiO 3 piezoceramics. Materials Research Bulletin. 2015;68:260-266


[34] Chan W-H, Xu Z, Zhai J, Chen H. Uncooled tunable pyroelectric response of antiferroelectric Pb0. 97La0. 02 (Zr0. 65Sn0. 22Ti0. 13) O3 perovskite. Applied Physics Letters. 2005;87:192904


[40] Sebastian MT. Dielectric Materials for Wireless Communication. Amsterdam: Elsevier; 2010


[54] Roth RS. Classification of perovskite and other ABO3-type compounds. Journal of Research of the National Bureau of Standards. 1957;58: 75-88


[61] Parizi SS, Mellinger A, Caruntu G. Ferroelectric barium titanate nanocubes as capacitive building blocks for energy storage applications. ACS Applied Materials & Interfaces. 2014;6: 17506-17517


[64] Sakabe Y, Yamashita Y, Yamamoto H. Dielectric properties of nano-crystalline BaTiO3 synthesized by
Recent Advances in Multifunctional Perovskite Materials


[94] Kim J-S, Yoon S-G. High dielectric constant (Ba0. 65Sr0. 35) (Ti0. 41Zr0. 59) O3 capacitors for Gbit-scale dynamic random access memory devices. Journal of Vacuum Science & Technology B. 2000;18:216-220


Bardeen J, Cooper LN, Schrieffer JR. Theory of superconductivity. Physical Review. 1957;108:1175

Sleight AW. Superconductive barium-lead-bismuth oxides. Google Patents. 1976

Xu Y. Ferroelectric Materials and their Applications. Amsterdam: Elsevier; 2013


Valasek J. The early history of ferroelectricity. Ferroelectrics. 1971;2:239-244

Scott WT. Erwin Schrödinger. Amherst: Univ of Massachusetts Press; 1967

Busch G. Early history of ferroelectricity. Ferroelectrics. 1987;74:267-284

Kingery WD, Lense E. High technology ceramics: Past, present, and future: The nature of innovation and change in ceramic technology. American Ceramic Society. 1986

Von Hippel A, Breckenridge RG, Chesley F, Tisza L. High dielectric constant ceramics. Industrial & Engineering Chemistry. 1946;38:1097-1109


Kittel C. Introduction to Solid State Physics. New Jersey: Wiley; 2005


[133] Ederer C, Spaldin NA. Influence of strain and oxygen vacancies on the


[171] Zener C. Interaction between the d-shells in the transition metals. II. Ferromagnetic compounds of manganese with perovskite structure. Physical Review. 1951;82:403

[172] Li X, Zheng R, Li G, Zhou H, Huang R, Xie J, et al. Jahn-Teller effect and stability of the charge-ordered state in La 1−x Ca x MnO3 (0.5≤ x≤ 0.9) manganites. EPL (Europhysics Letters). 2002;60:670


