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A Study of Synthesis, Charactionzation of Perovskite Material

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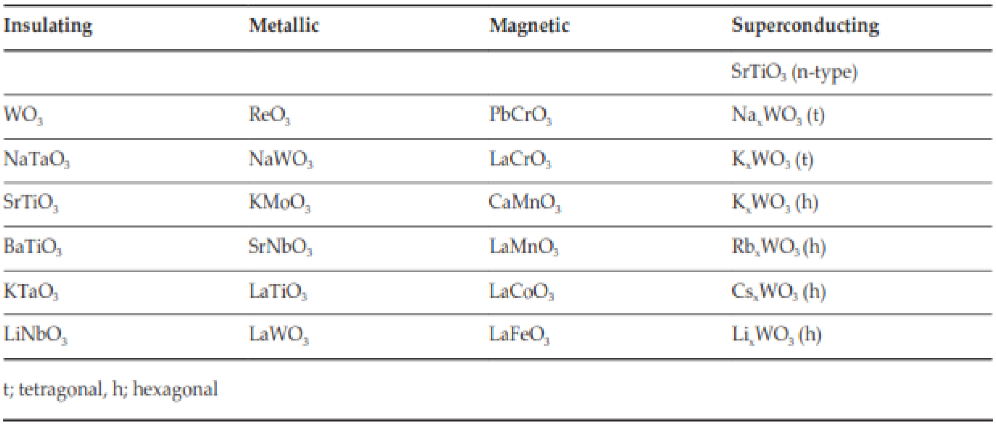
ABSTRACT

Inorganic perovskite-type oxides are fascinating nanomaterials for wide applications in catalysis, fuel cells, and electrochemical sensing. Perovskites prepared in the nanoscale have recently received extensive attention due to their catalytic nature when used as electrode modifiers. The catalytic activity of these oxides is higher than that of many transition metals compounds and even some precious metal oxides. They exhibit attractive physical and chemical characteristics such as electronic conductivity, electrically active structure, the oxide ions mobility through the crystal lattice, variations on the content of the oxygen, thermal and chemical stability, and super - magnetic, photocatalytic, thermoelectric, and dielectric properties. Nanoperovskites have been utilized as catalysts in oxygen reduction and hydrogen evolution reactions exhibiting high electrocatalytic activity, lower activation energy, and high electron transfer kinetics. In addition, some perovskites are promising candidates for the development of effective anodic catalysts for direct fuel cells showing high catalytic performance. Moreover, they are recently utilized in electro - chemical sensing of alcohols, gases, glucose, H2O2 , and neurotransmitters. They can enhance the catalytic performance in terms of selectivity, sensitivity, unique long-term stability, excellent reproducibility, and anti-interference ability. In addition, organo - metallic halide perovskites exhibited efficient intrinsic properties for photovoltaic solar cells exhibiting good stability and high efficiency.

1. Introduction

The mineral CaTiO3 was discovered by Geologist Gustav Rose in the Ural Mountains in 1839, and it was named perovskite in recognition beholden to Count Lev Alexevich von Perovski, an eminent Russian mineralogist [1–5]. The name perovskite represented any compound that has ABC3 formula where an octahedron of C ions surrounded the B ion. The Earth's crust contains various types of perovskites and the most abundant ones are MgSiO3 and FeSiO3 . Perovskite family includes several types of oxides like transition metal oxides with the formula ABO3 . Some examples of ABO3 perovskites and their corresponding properties are summar-ized in Table 1 [1, 2, 5].

Table 1. Some perovskites and corresponding properties



Insulating	Metallic	Magnetic	Superconducting
			$SrTiO_3$ (n-type)
WO_3	ReO_3	$PbCrO_3$	Na_xWO_3 (t)
$NaTaO_3$	$NaWO_3$	$LaCrO_3$	K_xWO_3 (t)
$SrTiO_3$	$KMoO_3$	$CaMnO_3$	K_xWO_3 (h)
$BaTiO_3$	$SrNbO_3$	$LaMnO_3$	Rb_xWO_3 (h)
$KTaO_3$	$LaTiO_3$	$LaCoO_3$	Cs_xWO_3 (h)
$LiNbO_3$	$LaWO_3$	$LaFeO_3$	Li_xWO_3 (h)

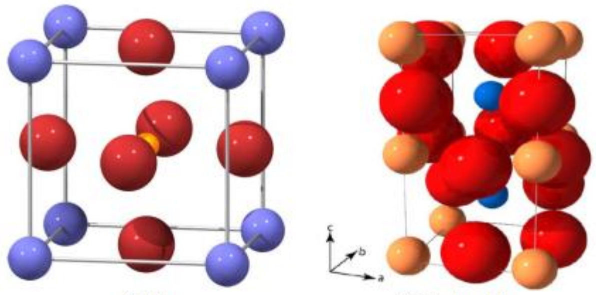
t; tetragonal, h; hexagonal

Perovskite oxides exhibit an array of electrical properties and a variety of solid-state phenom-ena from insulating, semiconducting, metallic, and superconducting characters; therefore, they are very fascinating to be studied and applied in a large scale. Many of ABO3 perovskites are cubic or nearly cubic in structure in their ideal form; however, one or more phase transitions may be achieved particularly at low temperature. In addition, many of them showed magnetic ordering and as a result, large variety of magnetic structures can be found. Some perovskites contained localized electrons, some contained delocalized energy-band states, and the behavior of other perovskites was a transition between these two types. The perovskite structures can incorporate ions of various size and charge showing great flexibility of compo-sition. Moreover, substitutions of ions into the A- and/or B-sites or deviation from ideal stoichiometry resulted in altering the electronic properties of the perovskites. Perovskites exhibit atomic arrangement in the form of 3-dimensional array of corner sharing octahedra. On the other hand, layered perovskites included 2-dimensional layers of corner sharing octahedral separated by cations layers. As a result, the electronic energy bands of perovskites and layered perovskites are very unusual and their structure is unique in properties [1, 2]. Perovskites displayed diversity of electric, optical, and magnetic properties because of the fact that 90% of the elements in the periodic table can be stable in the perovskite structure and the feasibility of partial substitutions of cations in A- and B-sites forming A1-xA′xB1-yB′yO3 [6]. Perovskites showed great interest in several applications due to their wide various and useful properties in photochromic, electro chromic, image storage, switching, filtering, and surface acoustic wave signal processing devices. They were utilized as catalytically active catalyst for several reactions like carbon monoxide and hydrocarbons oxidation, hydrogen evolutionreaction and nitrogen oxides, and oxygen reduction reactions. They also have a good impact in many electrochemical applications like sensing, bio sensing, photo electrolysis of water producing hydrogen, and fuel cells [1, 2].

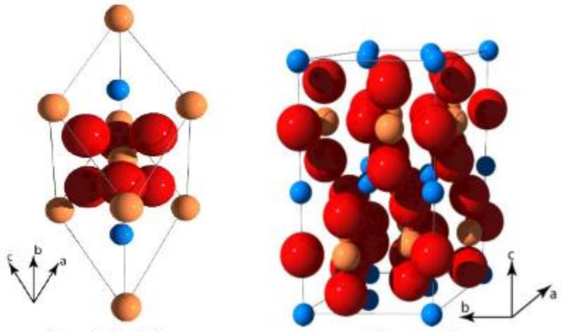
2. Crystallography of the Perovskite Structure

In the ABO_3 form, B is a transition metal ion with small radius, larger A ion is an alkali earth metals or lanthanides with larger radius, and O is the oxygen ion with the ratio of 1:1:3. In the cubic unit cell of ABO_3 perovskite, atom A is located at the body center, atom B is located at the cube corner position, and oxygen atoms are located at face-centered positions (Figure 1). The 6-fold coordination of B cation (octahedron) and the 12-fold coordination of the A cation resulted in the stabilization of the perovskite structure. The perfect perovskite structure was described by Hines et al. as corner linked BO_6 octahedra with interstitial A cations [1–10]. Some distortions may exist in the ideal cubic form of perovskite resulted in orthorhombic, rhombo-hedral, hexagonal, and tetragonal forms (Figure 1) [3–7]. Figure 2 represented the distortion from cubic perovskite to orthorhombic one. In general, all perovskite distortions maintaining the A- and the B-site oxygen coordination was achieved by the tilting of the BO_6 octahedra and an associated displacement of the A cation [4].

Generally, two requirements should be fulfilled for perovskite formation: 1. Electroneutrality; the perovskite formula must have neutral balanced charge therefore the product of the addition of the charges of A and B ions should be equivalent to the whole charge of the oxygen ions. An appropriate charge distribution should be attained in the forms of $A^{1+}B^{5+}O_3$, $A^{4+}B^{2+}O_3$ or $A^{3+}B^{3+}O_3$. 2. Ionic radii requirements; $r_A > 0.090$ nm and $r_B > 0.051$ nm, and the tolerance factor must have values within the range $0.8 < t < 1.0$ [2–8].

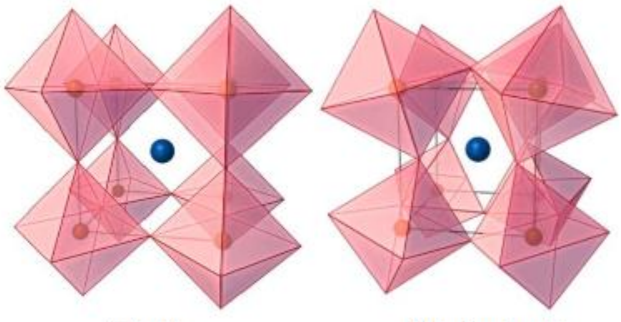


Cubic Orthorhombic



Rhombohedral Hexagonal

Figure 1. Different perovskite unit cells. Blue spheres represent the A cations, yellow spheres represent the B cations and red spheres represent oxygen anions forming an octahedral



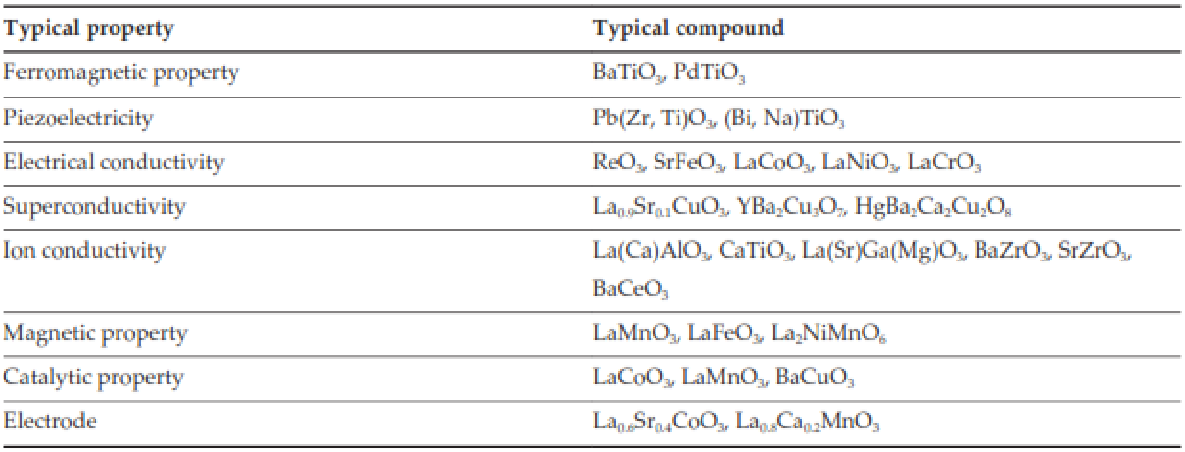
(a) cubic (b) orthorhombic

Figure 2. Perovskite distortion from (a) cubic to (b) orthorhombic

3. Typical Properties of Perovskites

Perovskite exhibited a variety of fascinating properties like ferroelectricity as in case of $BaTiO_3$ and superconductivity as in case of $Ba_2YCu_3O_7$. They exhibited good electrical con-ductivity close to metals, ionic conductivity and mixed ionic and electronic conductivity. In addition, several perovskites exhibited high catalytic activity toward various reactions. Table 2 contains a summary of typical properties of perovskites. Several typical properties will be discussed in this section like ferroelectricity, magnetism, superconductivity, and catalytic activity [9].

Table 2. Typical properties of perovskite oxides



Typical property	Typical compound
Ferromagnetic property	$BaTiO_3$, $PdTiO_3$
Piezoelectricity	$Pb(Zr, Ti)O_3$, $(Bi, Na)TiO_3$
Electrical conductivity	ReO_3, $SrFeO_3$, $LaCoO_3$, $LaNiO_3$, $LaCrO_3$
Superconductivity	$La_{0.9}Sr_{0.1}CuO_3$, $YBa_2Cu_3O_7$, $HgBa_2Ca_2Cu_2O_8$
Ion conductivity	$La(Ca)AlO_3$, $CaTiO_3$, $La(Sr)Ga(Mg)O_3$, $BaZrO_3$, $SrZrO_3$, $BaCeO_3$
Magnetic property	$LaMnO_3$, $LaFeO_3$, La_2NiMnO_6
Catalytic property	$LaCoO_3$, $LaMnO_3$, $BaCuO_3$
Electrode	$La_{0.6}Sr_{0.4}CoO_3$, $La_{0.8}Ca_{0.2}MnO_3$

1. Dielectric properties

There are some properties inherent to dielectric materials like ferroelectricity, piezoelectricity, electrostriction, and pyroelectricity. One of the important characteristic of perovskites is ferroelectric behavior, which is obvious in BaTiO3 , PdZrO3 , and their doped compounds. The ferroelectric behavior of BaTiO3 was strongly related to its crystal structure. BaTiO3 wassubjected to three phase transitions; as the temperature increases, it was converted from monoclinic to tetragonal then to cubic. At temperature higher than 303 K, BaTiO3 does not show any ferroelectric behavior as it crystallizes into cubic structure. BaTiO3 showed high dielectric constant based on the anisotropy of its crystal structure resulting in large dipole moment generation in BaTiO3 [9].

2. Electrical conductivity and superconductivity

One of the obvious properties of perovskites is superconductivity. Cu-based perovskites act as high-temperature superconductors, and La-Ba-Cu-O perovskite was first reported. The presence of Cu in B-site is essential for the superconductivity and various superconducting oxides can be manufactured with different A-site ions. Some examples of high temperature superconductors are YBa2Cu3O7 , Bi2Sr2Ca2Cu3O10, and HgBa2Ca2Cu3O8+δ with critical temper-ature of superconducting transition (Tc) of 130–155 K. The superconductivity is associated with the layers of Cu-O in Cu-based perovskites, and the Tc value is associated with the Cu-O layers number in the crystal lattice. The synthesis of 5 or more Cu-O-layered perovskites did not achieve successfully due to the low chemical stability. One of the highly significant supercon-ductors with great Tc value is YBa2Cu3O7 . In addition, the oxygen nonstiochiometry is one of the most significant reasons for the high value of Tc. In YBa2Cu3O7–δ , when the value of δ < 0.5, it crystallizes into orthorhombic structure, which is superconductive. For δ > 0.5, it showed a tetragonal structure that does not show any superconductivity. The crystal structure affected greatly the superconductivity in high Tc oxides, and as a result, high Tc values can be achieved by improving the chemical stability of the perovskite crystal structure. Furthermore, some perovskites exhibited great electronic conductivity similar to that of metals like Cu. LaCoO3 and LaMnO3 are examples of perovskites exhibiting high electronic conductivity, and therefore they are utilized as cathodes in solid oxide fuel cells displaying superior hole conductivity of 100 S/cm. The electronic conductivity of the perovskites can be enhanced by doping the A-site with another cation, which resulted in increasing the quantity of the mobile charge carriers created by the reparations of charge [9].

3. Catalytic activity

Perovskites showed excellent catalytic activity and high chemical stability; therefore, they were studied in a wide range in the catalysis of different reactions. Perovskites can be described as a model of active sites and as an oxidation or oxygen-activated catalyst. The stability of the perovskite structure allowed the compounds preparation from elements with unusual valence states or a high extent of oxygen deficiency. Perovskites exhibited high catalytic activity, which is partially associated with the high surface activity to oxygen reduction ratio or oxygen activation that resulted from the large number of oxygen vacancies. Perovskites can act as automobile exhaust gas catalyst, intelligent automobile catalyst and cleaning catalyst, etc., for various catalytic environmental reactions. It was reported in the literature that perovskites containing Cu, Co, Mn, or Fe showed excellent catalytic activity toward the direct decompo-sition of NO at high temperature, which is considered one of the difficult reactions in the catalysis (2NO → N2+O2). Perovskites showed superior activity for this reaction at hightemperatures because of the presence of oxygen deficiency and the simple elimination of the surface oxygen in the form of a reaction product. NO decomposition activity was enhanced upon doping. Also, under an atmosphere that is rich with oxygen up to 5%, Ba(La)Mn(Mg)O3 perovskite exhibited superior activity toward the decomposition of NO [9].Perovskite showed a great impact as an automobile catalyst; intelligent catalyst. Pd-Rh-Pt catalysts was utilized as an effective catalyst for the removal of NO, CO and uncombusted hydrocarbons. There is another catalyst that consists of fine particles, with high surface-tovolume ratio, and can be utilized to reduce the amount of precious metals used. However, these fine particles exhibited very bad stability under the operation conditions leading to catalyst deactivation. Therefore, perovskite oxides can be used showing redox properties to preserve a great dispersion state. Upon oxidation, Pd is oxidized in the form of LaFe0.57Co0.38Pd0.05O3 and upon reduction; fine metallic particles of Pd were produced with radius of 1–3 nm. This cycle resulted in partial replacement of Pd into and sedimentation from the framework of the perovskite under oxidizing and reducing conditions, respectively, displaying a great dispersion state of Pd. Also, this cycle improved the excellent long-term stability of Pd during the pollutants removal from the exhaust gas. Exposing the catalyst to oxidizing and reducing atmosphere resulted in the recovery of the high dispersion state of Pd. This catalyst is known as intelligent catalyst because of the great dispersion state of Pd and the excellent stability of the perovskite structure [9].

4. Methods of Perovskite Synthesis

1. Solid-state reactions

In solid-state reactions, the raw materials and the final products are in the solid-state therefore nitrates, carbonates, oxides, and others can be mixed with the stoichiometric ratios. Perovskites can be synthesized via solid-state reactions by mixing carbonates or oxides of the A- and Bsite metal ions corresponding to the perovskite formula ABO3 in the required proportion to obtain the final product with the desired composition. They are ball milling effectively in an appropriate milling media of acetone or isopropanol [11, 12]. Then the obtained product is dried at 100 °C and calcined in air at 600 °C for 4–8 h under heating/cooling rates of 2 °C/min. After that, the calcined samples are ground well and sieved. Then it was calcined again at 1300– 1600 °C for 5–15 h under the heating/cooling rate of 2 °C/min to confirm the formation of single phase of perovskite. Again grinding and sieving was carried out for the calcined samples [11, 13, 14]. The synthesis of BaCeO3 -based proton conductor perovskites [13] and BaCe0.95Yb0.05O3−δ [11] was achieved through the previous methodology using BaCO3, CeO2, and Yb2O3 as the starting materials and isopropanol as the milling media [10].

2. Gas phase preparations

Gas phase reaction or transport can be used for the deposition of perovskite films with a specific thickness and composition. Laser ablation [15], molecular beam epitaxy [16], dc sputtering [17], magnetron sputtering [18], electron beam evaporation [19], and thermal evaporation [20]techniques were developed for gas phase deposition. Gas phase deposition can be categorized into three types: (i) deposition at a low substrate temperature then postannealing at high temperature, (ii) deposition at an intermediate temperature of 873 to 1,073 K then post annealing treatment, and (iii) deposition at the crystallization temperature under suitable atmosphere. YBa2Cu3O7 films can be synthesized by the evaporation of Y, Cu, and BaF2 then annealing at high temperatures in O2 atmosphere wet with water vapor to reduce the annealing time and substrate interaction [20].

3. Wet chemical methods (solution preparation)

These methods included the sol-gel preparation, coprecipitation of metal ions using precipi-tating agents like cyanide, oxalate, carbonate, citrate, hydroxide ions, etc., and thermal treatment [21], which resulted in a single-phase material with large surface area and high homogeneity. These methods presented good advantages such as lower temperature com- pared to the solid-state reactions, better homogeneity, greater flexibility in forming thin films, improved reactivity and new compositions and better control of stoichiometry, particle size, and purity. Therefore, they opened new directions for molecular architecture in the synthesis of perovskites. Solution methods were classified based on the means used for solvent removal. Two classes were identified: (i) precipitation followed by filtration, centrifugation, etc., for the separation of the solid and liquid phases and (ii) thermal treatment such as evaporation, sublimation, combustion, etc., for solvent removal. There are several factors must be taken in consideration in solution methods like solubility, solvent compatibility, cost, purity, toxicity, and choice of presumably inert anions [10].

5. Doping of Perovskites

The different properties of perovskites and their catalytic activity are highly affected by the method of synthesis, conditions of calcination (time, atmosphere, fuel, temperature, etc.), and A- and/or B-site substitutions. The catalytic activity of the perovskite is highly affected by partial or total substitutions on A- and/or B-site cations because of the oxidation state modifi- cation, the variation of the chemical state of the elements at A- and/or B-site, the generation of oxygen vacancies, the mobility of oxygen lattice, and the formation of structural defects [58– 60]. The powerful bond between the B-site metal ions and the oxygen ions can be used to determine the basic characters of perovskites, and as a result, the B-site cation is responsible for the perovskite catalytic activity [61, 62]. Therefore, partial substitution of B-site cation with other metals M in AB1-yMyO3 will display the properties of both metals: the main metal B and the dopant one M [62]. On the other hand, the cation A can stabilize the unusual oxidation states of B-site cations by the controlled formation of crystal lattice vacancies, which lead to different catalytic performances [61]. Upon doping A- and/or B-sites in ABO3 perovskite oxides, the catalytic activity, ionic and electronic conductivity, and flexible physical and chemical properties can be altered for utilization in various applications [63–66]. Different cations with different sizes and charges can be hosted in the A- and B-sites of these perovskites; thus, many studies can be performed to utilize doped perovskites in various applications. Multiple cationic substitutions can be accepted in the stable perovskite lattice provided that Goldschmidt tolerance factor ranged between 0.75 and 1 and electroneutrality are preserved [59, 67, 68]. Therefore, variable amounts of different structural and electronic lattice defects can be accommodated in the perovskite structure as a result of their nonstoichiometry. This will further affect the activity of the perovskite and stabilize the unusual valence states of different metal ions [61, 67]. Some physical characteristics of perovskite-type oxides seriously associated with structural charac-ters were affected greatly by the structural deformations from the ideal cubic structure of the perovskite [69].

6. Conclusion

Inorganic perovskite-type oxides are excellent nano-materials for wide applications in catalysis, fuel cells, and electrochemical sensing, exhibiting attractive physical and chemical character-istics. They showed electronic conductivity, electrically active structure, the oxide ions mobility through the crystal lattice, variations on the content of the oxygen, thermal and chemical stability and super magnetic, photo catalytic, thermoelectric, and dielectric properties. Nano-perovskites have been utilized as catalysts in oxygen reduction and hydrogen evolutionreactions exhibiting high electro catalytic activity, lower activation energy and high electron transfer kinetics. In addition, some perovskites are promising candidates for the development of effective anodic catalysts for direct fuel cells showing high catalytic performance. Moreover, they are recently utilized in electrochemical sensing of alcohols, gases, glucose, H2O2, and neurotransmitters. They can enhance the catalytic performance in terms of unique long-term stability, sensitivity, excellent reproducibility, selectivity, and anti-interference ability. In addition, organometallic halide perovskites exhibited efficient intrinsic properties to be utilized as a photovoltaic solar cell with good stability and high efficiency.

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