ISSN: 0974-5823 Vol. 7 No. 7 July, 2022

International Journal of Mechanical Engineering

Review: Perovskite Materials, Properties, and their Multifunctional Applications

Sushmita Gupta[1*], Samarveer Singh [1], Ritu Rani Chaudhary[2], DeepShikha[1] and Vikky Singh[1]

[1]Department of Applied Chemistry

F.E.T., M.J.P.R. University, Bareilly, India

[2]B.S.A. College, Mathura, India

Abstract:

The perovskite material with the general formula ABX_3, where A = large cation, B = smaller cation and X = halogen or oxygen, have distinct physical properties. They are useful in ambipolar charge transfer, high value to absorption coefficient, specific high dielectric constant, low value of exciton and binding energy, magento resistant (MR) properties, ferroelectric features, pyroelectric, di-electric and piezoelectric character as well as designing materials for LED, biosensors, wave guided and field effect transistors etc. The present review includes the wide spread applications of the perovskite materials.

Keywords: Perovskite, catalyst, sensor, solar cell, application.

1. Introduction:

Perovskite materials are versatile in physical and chemical properties .These materials have very flexible structural probabilities and therefore show variety of electrical and magnetic behavior. Their wide spread applications involve multidisciplinary subject fields including electronic industrial uses, energy related applications and various fields of sensors, biosensors, catalysts as well as in opto electric and photochromic uses.

The general formula for the perovskiteis ABX_3, were A and B are cations and X is either oxygen or halogen. On this basis they belong to either perovskite oxide or perovskite halide family.

The first perovskite $CaTiO_3$ was discovered by Gustav Rose in 1839 and the name perovskite was given on the name of the famous scientist Count Le Alexerch von Perovski [1-3]. Perovskite materials have been reported to show insulator, metallic, semiconductor and superconductor activity. They have applications [4] in the fields of photochromic, electrochromic, optical, surface acoustic wave signal processing, switching and filtering devices. The catalyst industrial uses of perovskite materials include heterogeneous catalysis of nitrogen oxide reductions [5-8]. These compounds are used in automobile exhaust gas catalyst for selective removal of pollution from gaseous mixtures and therefore called as cleaning catalyst. The oxygen evolution reactions and oxygen reduction reactions are also catalyzed by perovskite materials and have used in rechargeable batteries, electrolysis of water, synthesis of organic compounds and fuel cells[9]. These compounds are also used in hydrogen evolution reactions. A full gamut of work has been done in the field of sensor and biological sensors [10,11]. Several works have been reported on the application of perovskite as neurotransmitter sensor, gas sensor . The area of fuel cell and solar cell research has also benefited by the perovskite materials. The metal halide pervokite are well known for their opto-electronic and photo voltaic applications [12].

2. Properties and applications of Perovskite materials

2.1 Electrical Applications

The various applications of perovskite are based on their structural beauty. The capacity of substitution of perovskite cation at A and B sites make them useful for engineering in their properties by making changes in the structure. Fig. 1 shows various electrical applications (Fig.1 & Table 1).

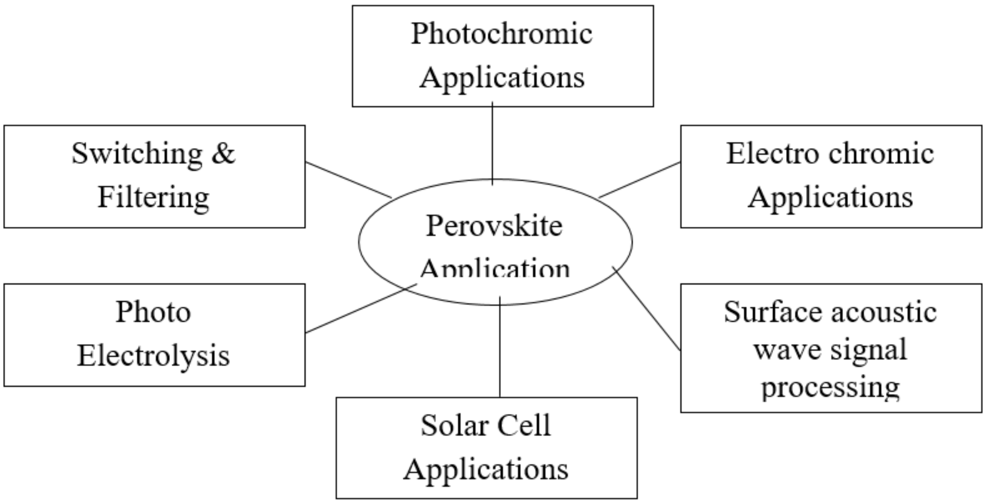

Fig. 1: Electrical Applications of Perovskite

Perovskite materials of different electrical nature have been synthesized and studies. Starting from insulating nature, metallic to superconducting compounds have been reported (Table-1)

S. No.	Property	Compounds
1.	Insulator	$SrTiO_3$, $BaTiO_3$, $KTaO_3$, $NaTaO_3$, $LiNbO_3$, WO_3
2.	Metallic	$SrNbO_3$, $LaWO_3$, $NaWO_3$, $KMOO_3$, $LaTiO_3$, $LaCoO_3$, $LaCrO_3$, ReO_3, $LaNiO_3$
3.	Super Conducting	$SrTiO_3$, $YBa_2Cu_3O_7$, $LiWO_3$, $La_{0.9}Sr_{0.1}CuO_3$, Hg Ba_2Ca_3Cu, $Bi_2Sr_2Ca_2Cu_2O_{10}$,
4.	Ionic Conductivity	$La(Ca)AlO_2$, $CaTiO_3$, $La(Sr)Ga(Mg)O_3$, $BaZrO_3$, $SrZrO_3$, $LaCoO_3$, $BaCeO_3$,$LaMnO_3$
5.	Electrode	$La_{0.5}Sr_{0.4}CoO_3$, $La_{0.8}Ca_{0.2}MnO_3$

Table-1 : Specific electrical properties of different Perovskites

Perovskite La-Ba-Cu-O was the first reported high temperature superconductor. The specific features of this super conductor Perovskite materials is that it has copper ion in B site and at A site, the transition metals are present. For $YBa_2Cu_3O_7$ the superconductivity transition temperature is 130K.

2.1. Catalytic applications

Nano perovskite materials are useful in electro catalytic oxygen reduction and hydrogen evolution process. The low energy of activation and high electron transfer makes them promising performer as anodic catalyst for fuel cells.The following features are important for a perovskite to act as catalyst:

(i) They have model structure and have active sites.

(ii) They should be chemically stable.

(iii) They should behave as oxygen activated catalyst.

(iv) They must be able to stabilize unusual valence of different elements.

(v) High surface activity of perovskite is generally related with the enormous oxygen deficiency in the structure.

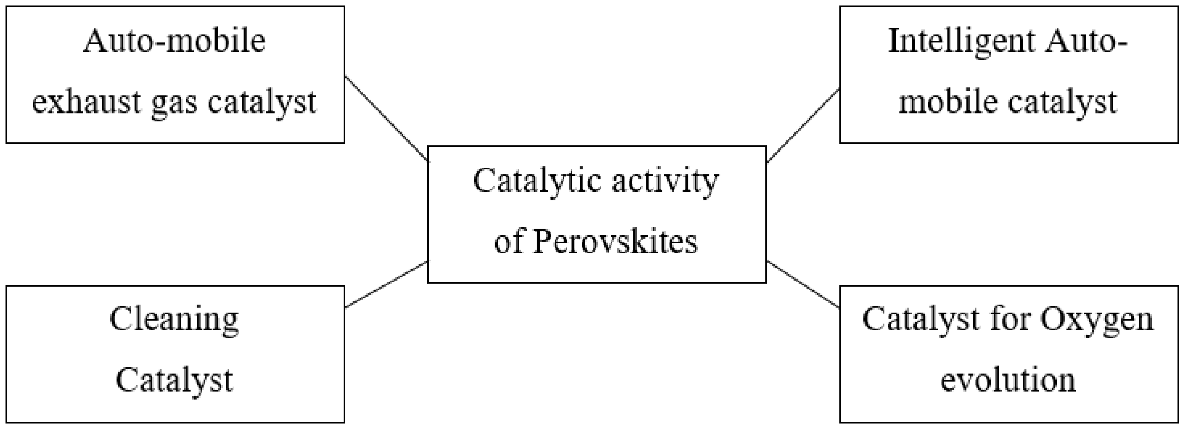

Fig-2: Sketch diagram for the catalytic activity of perovskite

2.1.1. Auto-mobile exhaust gas catalyst

In heterogeneous catalysis, perovskite can be used as catalyst in nitrogen, oxides storage and reduction (NSR), selective catalytic reduction (SCR) and hybrid (NSR-SCR) technique for removal of NOx from the exhaust gas [9]. The use of nobel metal catalyst is costly but by the application of perovskite (e.g. 0.5% Pd – 30% $La_{0.5}$ $B_{0.5}$ CoO_9/Al_2O_3 catalyst) gives the 92% conversion result for NOx to nitrogen. Catalyst containing copper, cobalt, manganese and iron perovskite have been reported to exhibit wonderful catalytic activity for the decomposition of nitrogen oxide.

$$2NO \rightarrow N_2 + O_2$$

In perovskite the simple deficiency of oxygen and elimination of surface oxygen as reaction product facilitate the reaction at high temperature.

2.1.2. Intelligent Catalyst

Removal of nitrogen oxides, carbon mono oxide and hydrocarbon of uncombusted state can be removed from the polluted gas with the help of Pd-Rh-Pt based catalysts. The catalysts of high surface area with respect to volume in fine particles of precious metals are generally used but in fine particles form, they have very low stability and can cause deactivation of catalyst activity. In $LaFe_{0.57}CO_{0.38}Pd_{0.05}O_3$ which have redox property and dispersion ability both. The fine Pd particles were produced during the reduction process. This cyclic procedure results the partial replacement of palladium in the structural framework of perovskite during redox reaction. This provides the dispersed state of palladium and makes the process economic. Therefore, it is called as intelligent catalyst.

2.1.3. Cleaning Catalyst

The removal of pollutants like NO, CO and unburned hydrocarbon gases can be done with the help of Perovskite based materials (Fig-3).

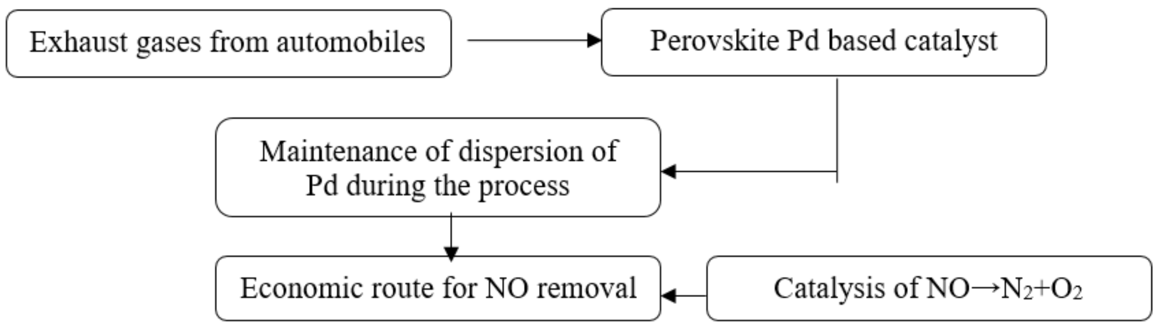

Fig-3 Systematic representation for action of cleaning catalyst

2.1.4. Oxygen evolution reactions (OER) and Oxygen reduction reactions(ORR)

These reactions are useful in many industrial applications [13-15] like water electrolysis, rechargeable batteries, fuel cells, electro winning, organic synthesis etc. The commonly used catalyst for these reactions are costly.they are made up precious metal oxide .Therefore it became important to develop catalyst based on rare earth or transition metal oxides of low cost. The characteristic features of perovskite catalyst are as follow:

(i) They have specific electric and magnetic properties.

(ii) Structure with defects.

(iii) Presence of disorder free oxygen vacancies for improved oxygen ion mobility.

(iv) Better cation ordering in structure.

The Table-2 shows the importance of perovskite in OER and ORR reactions.

S.No.	Perovskite	Method of Preparation	Medium	Specific features
1.	$Ba_{0.5}Sr_{0.3}Co_{0.8}Fe_{0.2}O_3$	Sol gel	KOH	Higher catalytic activity for OER than normal unmodified electrode
2.	$LaFeO_3$	Microwave assisted synthesis	$HClO_4$	100 times better catalytic activity than normal electrode for OER
3.	$La_{0.6}Ca_{0.4}CoO_3$	Sol- gel method	Basic medium	High surface area and high conductivity

Table-2 : Catalytic activity in OER and ORR reactions of perovskite materials

2.1.5. Hydrogen evolution reactions (HER)

In the group of renewable and clean energy resources, the hydrogen is considered as a very good fuel. The importance of hydrogen evolution reactions (HER) have been observed in hydrogen oxygen reaction in fuel cells, energy storage via hydrogen generation and also in electro deposition and corrosion of metal in acids. For the catalytic requirement of HER, it is necessary that the catalyst must have catalytic capability with proper surface to volume ratio and good range of stability. In HER reactions first step involves the removal or proton and in the second step desorption or recombination of proton takes place (Fig. 3).

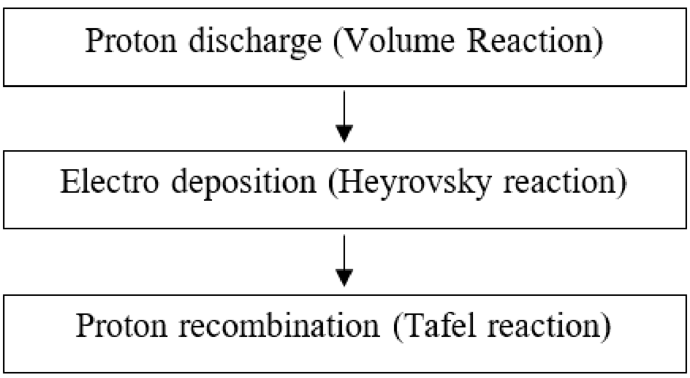

Fig-3 : Steps during the HER reactions

Various perovskites e.g. $LaFeO_3$, $SnFeO_3$, $NdFeO_3$, $GdFeO_3$, $SrPdO_3$, $LaNiO_3$, $LaMnO_3$, $SrRuO_3$ and $CaRuO_3$ have been reported to show good catalytic activity for HER reactions. The exchange current densities at constant over potential and activation energies have been measured.

2.2. Quantum paraelectrics

Some perovskite substances like $SrTiO_3$, $KTaO_3$, $CaTiO_3$ show quantum para electric [16,17] property i.e. the potency of the material to show the behavior of phase transition at low temperature (the temperature should be low for production of quantum effect). The ultra high melting point materials $Ba(Mg_{1/3}\ Ta_{2/3})O_3$ a very small quantity of impurity incorporation makes the perovskite to exhibit ferroelectric property.

2.3. Giant magneto resistance (GMR) or colossal magneto resonance (CMR)

The change in resistance by more than ten times on applying the magnetic field was observed in perovskite based substances e.g. $R_{1-x}A_xMnO_{3+7}$ (R= rare earth element: Sr, Ca etc. The K_2NiF_4 are potential substances for synthesizing GMR, materials. These materials are useful in high pressure pump, damage analysis, in sensors and under water sonar systems.

2.4. Applications as sensor

2.4.1. Neurotransmitters sensor activity

The electrochemical determination of dopamine in the biological systems can be done by the nano perovskite carbon paste composite electrode. The carbon paste electrodes for the simultaneous analysis of uric acid, dopamine and ascorbic acid have been reported. La FeO_3 micro and nano sphere based electrode are used for the detection of neurotransmitter dopamines [18]. The glassy carbon electrode fabricated by self assembled perovskite microsphere made up of $LaFeO_3$nano sphere.

2.4.2. Gas Sensor

Perovskite materials based on lanthanum, strontium and samarium e.g. $LaCoO_3$, $LaFeO_3$, $LaPbCuD_3$, $LaGeCoO_3$, $LaPbFeO_3$, $LaMgFeO_3$, $SrFeO_3$, $LaMnO_3$, $SmFeMgO_3$, $LaBaFeO_3$, $LaCoFeO_3$, $SrTiFeO_3$, $NdFeO_3$, $LaFeO_3$, $SmFeO_3$ are reported as gas sensor for detection of CO, NO_2, methanol, ethanol and hydrocarbons [19,20].

2.4.3. Glucose and H_2O_2sensors

Determination of glucose and hydrogen peroxide is important in food and biomedical[21,22] fields. $SrPdO_3$ and $LaTiO_3$ are used for glucose while $LaNiTiO_3/CoFe_2O_4$ is used for detection of H_2O_2.

2.4.4. Perovskite based solar cells

Perovskite based photovoltaic cells [23] with methyl ammonium lead halide hybrid material has been created much attention by researchers. The important features of perovskite halides are as follow:

(i) Band gap between 1 to 2eV.

(ii) Good range of absorption coefficient, when used as sensitizer.

(iii) Good mobility of charge carriers.

(iv) Practicable method of preparation.

The commonly used lead based perovskite $CH_3NH_3PbI_3$ are toxic in nature. To improve this situation perovskite of other group IV metal halide nano crystals have been synthesized the toxicity, moisture sensitivity and stability problems are under consideration of researchers.

3. Conclusion

Perovskite oxides exhibit a wide spread characteristics and multi directional applications in electric fields, catalysis and sensors. Metal halide nanocrystals are important because of their applications in photo chromic, electronics and photo voltaic cells. The future prospective of these perovskite materials is also very promising in these fields. The drawback related to stability of these materials is under consideration among researchers working in this area. There is very much hope for better performance of the metal perovskite oxides and perovskite metal halides. The ferroelectric, piezo electric behaviours are very much interesting. Double perovaskite solar cells are very promising field for future research. The non toxic and stable perovskite solar cell will be coming soon with high performance efficiency.

Acknowledgement

The author is grateful for financial assistance from 'Research and Development Program', U.P. Govt. India.

REFERENCES

1. Wolfram T, Ellialtioğlu S. Electronic and Optical Properties of d-band Perovskites. 1st ed. Cambridge University Press: New York; 2006. 1 p.
2. Galasso FS. Structure, Properties and Preparation of Perovskite-Type Compounds. In: Smoluchowski R, Kurti N, editors. 1st ed. Pergamon Press: New York; 1969. p. 3–49. Chapter 2.
3. Ali SMM. Synthesis of Nano-particles Using Microwave Technique, the Study of their Physical Properties and Some Applications [PhD thesis]. Faculty of Science Cairo University; 2009.
4. Ishihara T. Perovskite Oxide for Solid Oxide Fuel Cells, Fuel Cells and Hydrogen Energy. In: Ishihara T, editor. Springer Science Business Media, LLC; 2009. p. 1–16. Chapter 1.
5. Atta NF, Galal A, Ali SM. The catalytic activity of ruthenates ARuO3 (A= Ca, Sr or Ba) for the hydrogen evolution reaction in acidic medium. International Journal of Electrochemical Science. 2012;7:725–746. DOI: 71772857.
6. 164.Jin C, Cao X, Lu F, Yang Z, Yang R. Electrochemical study of $Ba_{0.5}Sr_{0}.5Co_{0.8}Fe_{0.2}O_{3}$ perovskite as bifunctional catalyst in alkaline media. International Journal of Hydrogen Energy. 2013;38:10389–10393. DOI: 10.1016/j.ijhydene.2013.06.047.
7. 165.Malkhandi S, Manohar AK, Yang B, Prakash GKS, Narayanan SR. Properties of calcium-doped lanthanum cobalt oxide perovskite electrocatalysts for oxygen evolution in alkaline medium. The Electrochemical Society. Abstract 292, 220th ECS Meeting. 2011.
8. Kahoul A, Hammouche A, Nâamoune F, Chartier P, Poillerat G, Koenig JF. Solvent
9. Haile SM. Fuel cell materials and components. ActaMaterialia. 2003;51:5981–6000. DOI: 10.1016/j.actamat.2003.08.004.
10. Ghasdi M, Alamdari H. CO sensitive nanocrystalline LaCoO3 perovskite sensor prepared by high energy ball milling. Sensors and Actuators B. 2010;148:478–485. DOI: 10.1016/j.snb.2010.05.056.
11. Wang G, Sun J, Zhang W, Jiao S, Fang B. Simultaneous determination of dopamine, uric acid and ascorbic acid with LaFeO3 nanoparticles modified electrode. MicrochimActa. 2009;164:357–362. DOI: 10.1007/s00604-008-0066-6.
12. Bao X, Wang Y, Zhu Q, Wang N, Zhu D, Wang J, Yang A, Yang R. Efficient planar perovskite solar cells with large fill factor and excellent stability. Journal of Power Sources. 2015;297:53–58. DOI: 10.1016/j.jpowsour.2015.07.081.
13. Atta NF, Galal A, Ali SM. The effect of the lanthanide ion-type in LnFeO3 on the catalytic activity for the hydrogen evolution in acidic medium. International Journal of Electrochemical Science. 2014;9:2132–2148. DOI: 94967196.
14. Ali SM, Abd Al-Rahman YM, Galal A. Catalytic activity toward oxygen evolution of LaFeO3 prepared by the microwave assisted citrate method. Journal of Electrochemical Society. 2012;159(9):F600–F605. DOI: 10.1149/2.063209jes.
15. Galal A, Atta NF, Darwish SA, Abd El Fatah AA, Ali SM. Electrocatalytic evolution of hydrogen on a novel SrPdO3 perovskite electrode. Journal of Power Sources. 2010;195:3806–3809. DOI: 10.1016/j.jpowsour.2009.12.091.
16. Malavasi L, Ritter C, Mozzati MC, Tealdi C, Islam MS, Azzoni CB, Flor G. Effects of cation vacancy distribution in doped LaMnO3+δ perovskites. Journal of Solid State Chemistry. 2005;178:2042–2049. DOI: 10.1016/j.jssc.2005.04.019.
17. Lin F, Shi W. Effects of doping site and pre-sintering time on microstructure and magnetic properties of Fe-doped BaTiO3 ceramics. Physica B. 2012;407:451–456. DOI: 10.1016/j.physb.2011.11.013.
18. Thirumalairajan S, Girija K, Mastelaro VR, Ganesh V, Ponpandian N. Detection of the neurotransmitter dopamine by a glassy carbon electrode modified with self assembled perovskite LaFeO3 microspheres made up of nanospheres. RSC Advances. 2014;4:25957–25962. DOI: 10.1039/C4RA03467H.

19. 141.Atta NF, Ali SM, El-Ads EH, Galal A. The electrochemistry and determination of some neurotransmitters at SrPdO3 modified graphite electrode. Journal of the Electrochemical Society. 2013;160(7):G3144-G3151. DOI: 10.1149/2.022307jes.
20. 142.Thirumalairajan S, Girija K, Ganesh V, Mangalaraj D, Viswanathan C, Ponpandian N. Novel synthesis of LaFeO3 nanostructure dendrites: a systematic investigation of growth mechanism, properties, and biosensing for highly selective determination of neurotransmitter compounds. Crystal Growth and Design. 2013;13:291−302. DOI: 10.1021/cg3014305
21. Jia F, Zhong H, Zhang W, Li X, Wanga G, Songa J, Cheng Z, Yin J, Guo L. A novel nonenzymatic ECL glucose sensor based on perovskite LaTiO3-Ag0.1 nanomaterials. Sensors and Actuators B. 2015;212:174–182. DOI: 10.1016/j.snb.2015.02.011.
22. Ye D, Xu Y, Luo L, Ding Y, Wang Y, Liu X, Xing L, Peng J. A novel nonenzymatic hydrogen peroxide sensor based on LaNi0.5Ti0.5O3/CoFe2O4 modified electrode. Colloids and Surfaces B: Biointerfaces. 2012;89:10–14. DOI: 10.1016/j.colsurfb.2011.08.014.
23. Yang Z, Cai B, Zhou B, Yao T, Yu W, Liu FS, Zhang W, Li C. An up-scalable approach to CH3NH3PbI3 compact films for high-performance perovskite solar cells. Nano Energy. DOI: 10.1016/j.nanoen.2015.05.027.