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Chapter 4

Perovskites-Based Nanomaterials for Chemical Sensors

Morteza Enhessari and Ali Salehabadi

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Abstract

The perovskite structure is adopted by many compounds in solid-state chemistry. The sensitivity, selectivity, and stability of many perovskite nanomaterials have been devoted the most attention for chemical sensors. They are capable to sense the level of small molecules such as O$_2$, NO, and CO. This chapter provides a comprehensive overview of perovskite nanoscale materials that concentrate on chemical sensors. The perovskite structure, with two differently sized cations, is amenable to a variety of dopant additions. This flexibility allows for the control of transport and catalytic properties, which are important for improving sensor performance. We devote the most attention on the synthesis, structural information, and sensing mechanism. We will later elaborate on the development mechanism of chemical sensors based on perovskite nanomaterials. We conclude this chapter with the personal perspectives on the directions toward future works on a novelty of nanostructured chemical sensors.

Keywords: Perovskite, Nanomaterial, Chemical sensor, Gas sensing material, Semiconductor

1. Introduction

The 3D-metal monooxides such as MnO, FeO, CoO, and NiO are semiconductors with low electrical conductivities. In general, the as-mentioned metal oxides have such large band gaps that they are insulators. The structure with general formula ABX$_3$, containing 12-coordinate hole of BX$_3$ is occupied by a large A ion (A: Ni, Pb, Fe, Co, Zn, etc) are known as perovskites. The tetragonal structure of perovskites showing the local displacements leads to the variation in electric behavior of this material (Figure 1).
Figure 1. The local ion displacements of a tetragonal ABX₃ structure [1].

Many applications of perovskites (here ABO₃) are reported in electrodes of solid oxide fuel cells [2], metal–air batteries [3], gas sensors [4], and high-performance catalysts [5].

Metal-oxide semiconductors, such as semiconducting tin oxide (SnO₂), have been used as chemical sensors for a number of years. Applications include environmental monitoring, fire detection, and vehicle monitoring [4]. The fundamental sensing mechanism of these metal-oxide-based gas sensors relies upon the change in electrical conductivity due to the interaction between the gases in the environment and oxygen in the grain boundaries.

A chemical sensor is a device that transforms chemical information into an analytically useful signal. The chemical information may originate from a chemical reaction of the analyte or from a physical property of the investigated system. They have applications in different areas such as medicine, home safety, environmental pollution, and many others. Chemical sensors are classified according to the operating principle of the transducer (Table 1).

A variety of chemical methods have been reported for the synthesis of semiconducting materials including perovskites, spinels, or ilminites which include ball-milling [6, 7], combustion synthesis [8–10], co-precipitation [11], sol–gel [12–15], radio frequency sputtering [16–19], solid-state reaction [20–22], and molten-salt method [23, 24].

In this chapter, we will review the routine reliable synthesis method, structural information, and gas sensing behavior of (mixed) metal-oxide semiconductors with tunable functionalities used in electrical devices for chemical sensors. Novel functional nanostructure semiconductors will be presented.
### Table 1. Classification of chemical sensors

<table>
<thead>
<tr>
<th>Type of chemical sensor</th>
<th>Source</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical (optodes)</td>
<td>Optical phenomena</td>
<td>Absorbance, reflectance</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Luminescence</td>
</tr>
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<td></td>
<td></td>
<td>Fluorescence</td>
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<tr>
<td></td>
<td></td>
<td>Opto-thermal effect</td>
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<tr>
<td></td>
<td></td>
<td>Light scattering</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>Electrochemical process</td>
<td>Voltammetric sensors</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Potentiometric sensors</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chemically sensitized field effect transistor potentiometric</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solid electrolyte gas sensors</td>
</tr>
<tr>
<td>Electrical</td>
<td>Electrical properties</td>
<td>Metal-oxide semiconductor</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Organic semiconductor</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electrolytic conductivity</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electric permittivity</td>
</tr>
<tr>
<td>Mass sensitive</td>
<td>Mass change at a specially modified surface</td>
<td>Piezoelectric devices</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Surface acoustic wave devices</td>
</tr>
<tr>
<td>Magnetic</td>
<td>Change of paramagnetic properties</td>
<td>Oxygen monitors</td>
</tr>
<tr>
<td>Thermometric</td>
<td>Heat effects of a specific chemical reaction or adsorption</td>
<td>Combustion reaction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Enzymatic reaction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Optothermal device</td>
</tr>
<tr>
<td>Radiation</td>
<td>Change of Physical properties</td>
<td>X-, p- or r-radiation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chemical composition</td>
</tr>
</tbody>
</table>

#### 1.1. Semiconductors chemistry

Semiconductors are insulators at absolute zero. Above this temperature and below the melting point of the solid, the metal acts as a semiconductor. Semiconductors are generally classified on the basis of their composition and particle size. Procreation of semiconductors with typical band gaps (a few eV’s corresponding to 100–200 kJ mol⁻¹) usually occurs between p-block metals and group 13/14 metalloids in combination with chalcogenides and pnictides [1].

Perovskites are an example of especial class of semiconductors (Figure 2). In this structure, the unit cell is not centrosymmetric and the crystal develops a permanent electric polarization as
a result of ion displacements (refer to Figure 1). Barium titanate, BaTiO$_3$, is one of the interesting examples of perovskite. This compound, at above 120°C, exhibits a cubic structure while a lower symmetry, that is, a tetragonal unit cell at room temperature due to ions displacement. Fe$_2$TiO$_5$ [25], NiTiO$_2$ [26, 27], CoTiO$_3$ [15, 28], BaZrO$_3$ [12], La$_2$CuO$_4$ [29], LaMnO$_3$ [5], MnTiO$_3$ [14], and PbTiO$_3$ [30] are some important examples of common perovskite oxide semiconductors.

Figure 2. Schematic representation of (a) perovskite (ABX$_3$) structure, (b) emphasizes of octahedral sites, and (c) its respective projection [1].

1.2. Semiconducting Chemical Sensors

Chemical sensors are generally classified according to the shape of metal oxides to nanotubes, nanorods, nanobelts, and nanowires [16]. A nanotube sensors include metal-oxide tubes such as Co$_3$O$_4$ (superior gas sensing capabilities toward H$_2$), SnO$_2$ (gas sensor to ethanol), and TiO$_2$ (hydrogen sensor). Nanorod-based sensors are involved in metal oxides such as ZnO, MoO$_3$, and tungsten oxide nanosensors, polymer nanorods such as poly(3,4-ethylene-dioxythiophene)-nanosensor, and metal nanorods such as Au nanosensor. As for nanobelt-based sensors, the attentions have been devoted on metal oxides such as ZnO (Co and O$_2$ sensors), SnO$_2$ (NO$_2$ sensors), and V$_2$O$_5$ (stable ethanol sensor) nanosensors, especially on ZnO nanobelts sensors. Nanowire metal oxides such as In$_2$O$_3$, SnO$_2$, ZnO, and Ga$_2$O$_3$ are used in NO$_2$ sensor, O$_2$ and CO sensors, NH$_3$ sensor, and ethanol sensor, respectively.

Perovskites with a general formula of ABO$_3$, a typical band gap of 3–4 eV and good thermal stability, are interesting choices for gas sensing materials [6]. A suitable material for a chemical sensor particularly gas sensors must not only have an appropriate electronic structure but also a good affinity with the target reactant which satisfies a number of other requirements such as manufacturability, hydrothermal stability, poisoning resistance, and adaptability with existing technologies. A wide variety of techniques are capable of synthesizing perovskites (nano)-materials. Sol–gel, impregnation, and precipitation are some of the most promising ones from efficiency and scale-up perspectives.

Many researchers have reported the gas sensing devices for dangerous gases such as carbon oxides (CO, CO$_2$), nitrogen oxides (NO, NO$_2$), and sulfur dioxide (SO$_2$) released from high-temperature combustion processes. CH$_4$ is another potent greenhouse gas that leads to global warming [31–34].
The perovskite oxide generally used in oxygen sensors is SrTiO$_3$ [35]. The oxygen partial pressure dependence of the conductivity of undoped SrTiO$_3$ contains both n-type and p-type regimes.

Gas sensing properties of nanocrystalline perovskite, LaFeO$_3$ [36] and BaTiO$_3$ [37], were successfully involved in previous literatures. It is concluded that the sensor based on the LaFeO$_3$ powders has a considerable sensing response to carbon dioxide. On the other hand, the BaTiO$_3$ sensor has a good selectivity to LPG against CO$_2$, H$_2$, NH$_3$, C$_2$H$_5$OH, and Cl$_2$. The BaTiO$_3$ thin films exhibit rapid response recovery which is one of the main features of this sensor. The defect structure and conduction properties of BaTiO$_3$ are also similar to those of SrTiO$_3$. However, the conductivity of BaTiO$_3$ is higher than that of SrTiO$_3$ in the p-type regime.

Hydrogen-sensitive semiconductor SrCe$_{0.9}$Yb$_{0.1}$O$_3$ nanopowders with tunable sensing functionalities toward H$_2$ and H$_2$S were synthesized in our group [13]. We observed a noticeable gas sensing behavior of the perovskite at room temperatures with semi-spherical and porous structures of nanoparticles.

High sensitivity and selectivity of mixed potential sensor based on Pt/YSZ/SmFeO$_3$ for NO$_2$ gas are investigated by Giang et al. [38]. They concluded that the high sensing performances of the as-mentioned sensor to NO$_2$ could be related to high catalytic active of the sensing material, that is, SmFeO$_3$. The adsorption of exposed gases on the surface of SmFeO$_3$ has been considered the factor that affects on the performance of the sensor Pt/YSZ-8/SmFeO$_3$.

CO sensitive nanocrystalline LaCoO$_3$ and La$_{1-x}$Ce$_x$CoO$_3$ perovskite sensor were investigated by Dhivia et al. [6] and Ghasdi et al. [31]. They inferred that the oxygen mobility increased by increasing the surface area. Moreover, the maximum response ratio of CO exhibited a good correlation with the total amount of desorbed oxygen.

Hydrocarbon gas sensing of nanocrystalline perovskite oxides, LnFeO$_3$ shows a superior response to gas sensing characteristics containing methane, propane, and n-hexane. Moreover, the rare earth elements of the as-mentioned perovskite play an important role to gas sensitivities [39].

Nanostructured perovskite, CdTiO$_3$ films for methane sensing, is one of the recent studied examples of semiconductor for chemical sensors [40]. The gas sensing mechanism of CdTiO$_3$ sensor is of surface-controlled type. The variation in the resistance of sensing material caused by the adsorption and desorption of gas molecules such as O$_2$. The oxygen adsorption on the CdTiO$_3$ film surface depends on the temperature. At high temperatures, O$_2$ dissociates into atomic oxygen O$_{\text{ads}}$(Eq. 1)

$$O_2(gas) \leftrightarrow O_{2(\text{ads})}$$
$$O_{2(\text{ads})} + e^- \rightarrow O_{2(\text{ads})}$$
$$O_{2(\text{ads})} + e^- \rightarrow 2O_{\text{ads}}$$
The chemistry image, the classification of perovskites applicable as gas sensing materials, the fabrications, and the performance mechanism of gas sensors will be discussed in the following sections. It must be noted that in this chapter the perovskites classes are named based on “B” site in general formula of ABO$_3$, such as stanate (BaSnO$_3$), titanate, and niobate.

2. Classification of perovskites

As mentioned before, the typical chemical formula of the perovskite structure is ABO$_3$ and AB$_2$O$_4$, where A and B denote two different cations. The ilmenite structure has the same composition as the perovskite, that is, ABO$_3$; however, A and B in this structure are cations of approximately the same size that occupy an octahedral site.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice parameter/× 10 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>Cubic structure</td>
</tr>
<tr>
<td>KTaO$_3$</td>
<td>3.989</td>
</tr>
<tr>
<td>NaTaO$_3$</td>
<td>3.929</td>
</tr>
<tr>
<td>NaNbO$_3$</td>
<td>3.949</td>
</tr>
<tr>
<td>BaMnO$_3$</td>
<td>4.040</td>
</tr>
<tr>
<td>BaZrO$_3$</td>
<td>4.193</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>3.904</td>
</tr>
<tr>
<td>KMnF$_3$</td>
<td>4.189</td>
</tr>
<tr>
<td>KFeF$_3$</td>
<td>4.121</td>
</tr>
<tr>
<td></td>
<td>Tetragonal structure</td>
</tr>
<tr>
<td>BiAlO$_3$</td>
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<td>PbSnO$_3$</td>
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<tr>
<td>BaTiO$_3$</td>
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<tr>
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</tr>
<tr>
<td>TiMnCl$_3$</td>
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<tr>
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<tr>
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<td>5.381</td>
</tr>
<tr>
<td>NaMgF$_3$</td>
<td>5.363</td>
</tr>
</tbody>
</table>

Table 2. Typical perovskite compound [41]
Various combinations of charged cations in the A and B sites of perovskite compounds such as 1 + 5 and 2 + 4 have been reported. However, a complex combinations are also investigated, such as M(B’\(_{1/2}\)B”\(_{1/2}\))O\(_3\), where M can be Pb or La, B’ can be Sc, Fe, Ni, or Mg and B”: Nb, Ta, Ru(IV), or Ir(IV). Typical perovskite compounds with various lattice structures are listed in Table 2.

In Table 3, the as-reported elements that can be incorporated within the perovskite structure are listed (Self-test: to be completed by the readers). It is obvious that almost all elements except noble gases can be occupied either A or B lattice structure in the perovskite lattice. The crystal structure of perovskites is dependent on the size and the nature of the A and B atoms. Simplifying the possible lattice interaction between elements forms a perovskite structure for gas sensing materials.

| B/A | Na | K | Rb | Ca | Sr | Ba | Y | La | Hf | Ag | Cd | Ln | H | Pb | Ce | Th | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | Th |
|-----|----|----|----|----|----|----|---|---|----|----|----|----|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Li  | ✓  | ✓  | ✓  | ✓  | ✓  | ✓  | ✓ | ✓ | ✓  | ✓  | ✓  | ✓  | ✓ | ✓  | ✓  | ✓  | ✓  | ✓  | ✓  | ✓  | ✓  | ✓  | ✓  | ✓  | ✓  | ✓  | ✓  | ✓  | ✓  | ✓  | ✓  | ✓  |

Table 3. (Self-test) elements that can occupy perovskite structure (ABO\(_3\), A\(_2\)B\(_2\)O\(_4\))

“✓” Represents the available, as-synthesized gas sensing perovskites; “*” corresponds to LaFeO\(_3\) [42].
Another class of perovskites forms by the replacement of B-site elements with a dopant. The as-mentioned structure with general formula $A_xMB_2O_9$ is called as superstructure perovskites. In fact, large differences in ionic radii lead to the formation of this huge structure. Here, M can be Fe, Co, Ni, Zn, or Ca like $BaSrTa_2O_9$. Moreover, a new class of superstructure perovskite is invented where the ordering of cation vacancies located on A sites: for example, $MNB_2O_9$ ($M$-La, Ce, Pr, Nb) and $MTa_2O_9$ ($M$-La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Y, Er).

Typical polymorphs of the perovskite structure are brownmillerite ($A_2B_2O_5$). This is oxygen deficient type of perovskite, the oxygen vacancy is ordered [41, 43]. In this structure, as the content of oxygen drops, the phase changes from the cubic perovskite to tetragonal, to orthorhombic, and finally to the brownmillerite structure. These phases are in fact a repeating sequence of octahedral and tetrahedral layers [44]. In the typical example of a non-stoichiometric ternary oxide such as $SrFeO_{2.5+x}$ ($0 < x < 0.5$), there is a series of phases that is derived from the perovskite structure. Stepwise dropping of the oxygen content, the phase changes from the cubic ($x = 0.5$) to tetragonal ($x = 0.35$), to orthorhombic ($x = 0.25$), and to the brownmillerite structure ($x = 0$) [43, 44]. The as-mentioned phenomenon can be observed clearly in the reaction isotherm profiles (Figure 3). In the regions where two phases co-exist, the $x$-value increases greatly for the small increase in oxygen pressure.

![Figure 3. Reaction isotherm of SrFeO$_{2.5+x}$ in a substituted SrFe$_{0.9}$Cu$_{0.1}$O$_{2.5}$]([44]).

Ruddelsden–Popper compounds are a group of perovskite with the general formula $(ABO_3)_nAO$ (Figure 4). Some examples of this structure are $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$. 


3. Sensing materials and mechanism

Sensor technology has widely distributed as a basic enabling technology in many instances. Many applications of sensing devices particularly in intelligent manufacturing processing have been reported ranging from assessing the integrity of aircraft to monitoring the environment for hazardous chemicals [45, 46]. The oxygen deficient crystal structure in semiconducting oxide materials is responsible for the change in resistance an oxide sensor [1]. This is due to the adsorbed surface species [41]. The reducing gas develops a shrink charge region which allows better charge movement.

A chemical/gas sensor provides an electrical/optical output in response to chemical and physical interactions with chemicals/gases. In particular, the gas sensors have been used for various industrial and/or safety applications and chemical such as a) determination of gas leakage [41, 47–49], novel LPG sensitive materials working in the entire range of least explosive limit (LEL) to upper explosive limit (UEL) [30–32]. Nanostructured perovskite materials can improve the sensing properties of the sensor due to high surface-to-volume ratio characteristics. Knowledge of nanoscale perovskite sensing materials have been achieved a great attraction to serve as a novel gas sensing materials at the lower working temperatures.

How does a sensing materials work? Band theory is a principle of chemical sensors technology which postulates that when atoms or molecules are aggregated in the solid state, the outer atomic orbitals are split into bonding and antibonding orbitals and mix to form two series of closely spaced energy levels. In general, in a gas sensor, the gas species react with metal-oxide particle surfaces thereby trapping electrons (Figure 5). This is the process of chemisorptions. A resistance layer from an electron-depleted space (cloud) charge on the n-type (the majority of charge carriers are electrons) particle surface or conducting layer from accumulated holes on the p-type (the positive holes being the majority of charge carriers) particle [50]. Continued
reaction between gas molecules and chemisorbed oxygen causes electrons to release from oxygen back to oxide. The current changes the electrical conductivity in the space charge layer. The conductivity increases in the case of n-type oxides, as a greater charge carrier (electron) concentration, and decreases in p-type oxides, as electrons recombine with holes. Time-by-time changing of conductivity in the space charge layer varies the overall electrical resistance of the oxide. Hence, the space (cloud) charge surrounding the bulk material directly influenced the sensitivity, that is, thicker the space charge layer higher the sensitivity. The change of sensor resistance depends on a type of metal-oxide semiconductors, here perovskites. The changes in sensor resistance upon exposure to the target gas/reducing gas in the cases of n-type and p-type perovskite sensors are reported by Choopon et al. [51] as illustrated in Figure 6.

Figure 5. Mechanism of gas sensing [50].

Figure 6. Change of sensor resistance upon exposure to the target gas [51].
4. Application of perovskite nanomaterials in gas sensor

Variety of component and high chemical stability are two important characteristic of perovskite nanomaterials applicable for catalysts in various reactions. It is impractical to consider the classification of perovskites without their applications in sensing devices. The advent of high-performance solid-state gas sensors has motivated several scientists in searching the new perovskite materials and investigating their gas sensing properties. In general, the perovskites are either oxidation catalysts or oxygen-activated catalysts as an alternative to catalyst containing precious metals, or a model for active sites. The stability of the perovskite structure allows the invention of new compounds with an unusual valence state of elements or a high extent of oxygen deficiency [41]. In Table 4, we summarize the as-reported perovskite nanomaterials in sensing device. We mentioned that the high catalytic activity of perovskite oxides is based on the high surface activity to oxygen reduction ratio or large number of oxygen vacancies in the particular structure. Among the various catalytic reactions studied, automobile exhaust gas, various pollutant gases such as H2S, and NH3, NOx decomposition reaction gas, hydrogen gas, methanol, and LP gas attract particular attention. The perovskite materials can be used as a thin film (nanocomposites) or nanopowders.

<table>
<thead>
<tr>
<th>Sensing materials</th>
<th>NOx</th>
<th>CH4</th>
<th>NH3</th>
<th>LPG</th>
<th>C2H5OH</th>
<th>Acetone</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
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<td>Titanate</td>
<td>SrTi0.65Fe0.35O3, PbZr0.2Ti0.8O3, BaTiO3, CdTiO3, Na2Ti3O7</td>
<td>Li1-xLa_xTiO3</td>
<td>[52–57]</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferrite</td>
<td>SrTi0.65Fe0.35O3, PbZr0.2Ti0.8O3, BaTiO3, CdTiO3, Na2Ti3O7</td>
<td>Co0.5Ni0.5Fe0.5O4, Mg0.5Zn0.5Fe2O4, BaFeO3, SrFeO3</td>
<td>NiFe2O4</td>
<td>[17, 58–62]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cobaltite</td>
<td>Bi2CO3O19, La1-xSr_xCO3</td>
<td>Na2CO3, Bi2Cu3O2, Cu2O, Bi2FeO2</td>
<td>[63–69]</td>
<td></td>
<td></td>
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<tr>
<td>Cobaltate</td>
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<td>[6, 35, 60, 65–68]</td>
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</tr>
<tr>
<td>Manganate</td>
<td>La1-xSr_xCoO3, SrCoO3, SrCeO3, BaSnO3</td>
<td>Y2O3, La2O3, CaO, Li2CO3, SnO3</td>
<td>[67, 70]</td>
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<tr>
<td>Cerate</td>
<td>SrCe0.65Eu0.35O3, SrCeO3, SrFeO3</td>
<td>BaCe0.65Eu0.35O3, La2O3, CaO, Li2CO3, SnO3</td>
<td>[9, 71–73]</td>
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<td>Niobate</td>
<td>FeNbO3</td>
<td>BaNbO3, FeNbO3</td>
<td>[74, 75]</td>
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<tr>
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<td>LaNiO3</td>
<td>[76]</td>
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<tr>
<td>Stanate</td>
<td>BaSnO3, ZnSnO3, ZnSnO3</td>
<td>Ba1-xNi_xSnO3, Ba1-xLa_xSnO3, ZnSnO3</td>
<td>[77–83]</td>
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<td>[20, 48, 84]</td>
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<td>Chromate</td>
<td>MgCr2O4</td>
<td>MgCr2O4</td>
<td>[85, 86]</td>
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<tr>
<td>Molybdate</td>
<td>Bi2MoO3, Bi2FeMoO3, Bi2FeO3</td>
<td>ZnMnO3, Bi2FeO3(MoO4)</td>
<td>[87–89]</td>
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<tr>
<td>Tungstate</td>
<td>Sn2WO6</td>
<td>ZnWO4, MnWO4, CoWO4, Sn2WO6, SnWO3</td>
<td>[90–96]</td>
<td></td>
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</table>
Sensing materials

<table>
<thead>
<tr>
<th>Sensing materials</th>
<th>NO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>CH&lt;sub&gt;4&lt;/sub&gt;</th>
<th>NH&lt;sub&gt;3&lt;/sub&gt;</th>
<th>LPG</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;OH</th>
<th>Acetone</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
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<td>Perovskite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Titanate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferrite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cobaltate</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Manganate</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickelate</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Stanate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Chromate</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Molybdate</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Tungstate</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Table 4. Gas sensing perovskite oxides

From Table 4, it is obvious that the various combinations of elements are used to produce the perovskite nanomaterials for the as-mentioned sensing devices. Among them, the humidity, LPG, ethanol, and pollution gases have been achieved a great attention.

Humidity measurement is one of the most significant issues in various areas of applications such as instrumentation, automated systems, agriculture, climatology, and GIS. Molybdate-, stanate-, and titanate-based perovskites are three powerful groups of materials used in this criterion. When perovskite oxides are exposed to moisture, interaction occurs in three stages: (a) a few water vapor molecules are chemisorbed at the neck of the crystalline grains on activated sites of the surface and form hydroxyl groups. As a result of this interaction, the hydroxyl group of each water molecule is adsorbed on metal cations and possesses high charge carrier density and strong electrostatic fields, and producing mobile protons. The protons migrate on the surface and react with the neighbor surface oxygen to form a second hydroxyl group. The chemisorbed layer is the first formed layer. (b) After chemical completion of the first layer, subsequent water vapor layers are physisorbed on the first-formed hydroxyl layer. After forming the first physisorbed layer, another water molecule adsorbs via double hydrogen bonding to two neighboring hydroxyl groups. This is continued to form multilayer. (c) By forming the more layers, a large amount of water molecules is physisorbed and bonded water vapor molecules become mobile and form continuous dipoles and electrolyte layers between the electrodes to generate dielectric constant and bulk conductivity. Figure 7 shows the layer by layer adsorption of humidity on the ceramic intelligent surface.
Ferrite and cobaltate/cobaltite are two main groups of materials used as active sites in CO sensing device. The mechanism of CO sensors is based on an anionic adsorption and the lattice oxygen atoms activities in the surface of perovskites ceramic. Here, the oxygen atoms are adsorbed and react with the available CO gases to form CO$_2$ and generate a free electron [114] of following types (Eq. 2):

$$O_{\text{ads}} + \text{CO} \rightarrow \text{CO}_2 + e^-$$
$$\text{CO}_2 \rightarrow \text{CO}^{\text{aq}} \rightarrow \text{CO}^{\text{ads}} + e^-$$
$$\text{CO}^{\text{ads}} + \text{O}_2 \rightarrow \text{CO}_2 + e^-$$
$$\text{CO} + \frac{1}{2} \text{O}_2 + V^{\text{aq}} + e^- \rightarrow \text{CO}_2 + O^{\text{aq}}$$

A possible mechanism of oxidation of CO by lattice oxygen ions on the surface of La-doped BaTiO$_3$ is shown in Figure 8.

Figure 8. Schematic representation of CO absorption.

LPG (LPG is a mixture of hydrocarbons like n-propane and n-butane), ethanol, and NH$_3$ sensors are another classes of perovskite-based sensing devices with a variety of applications. The sensing mechanism follows almost the same mechanism. When the perovskite sensor is exposed to air, O$_2$ adsorbs on the surface substrate and trap electrons from the conduction...
band of perovskites. This occurs due to the electronegativity of oxygen atom, negative-charged chemisorbed oxygen species, that is, $O^{2-}$ and $O^-$. As a result, the number of holes increased, the resistance decreased, and the concentration of available carrier achieves a higher value. By exposing the sensing materials to reducing gases, the gas molecules first reacted with the adsorbed oxygen, the carrier (holes) density depressed (due to electron donating nature of gases), and finally increasing the resistance. The reaction mechanisms of LPG (Eq. 3), ethanol (Eq. 4), and NH$_3$ (Eq. 5) [115] are the following:

$$
C_pH_{2p} + ((3p+1)O^{\text{ads}}) \rightarrow pCO_2 + (p+1)H_2O(g) + (3p+1)e^-
$$

(3)

$$
C_3H_4OH + 6O^{\text{ads}} \rightarrow 2CO_2 + 3H_2O + 6e^-
$$

(4)

$$
2NH_3 + 3O^{\text{ads}} \rightarrow N_2 + 3H_2O + 3e^-
$$

(5)

An example is LaCo$_{0.1}$Fe$_{0.9}$O$_3$ nanoparticles which used to investigate the ethanol sensing properties [116]. A careful consideration on the response curves indicates that the La-Co$_{0.1}$Fe$_{0.9}$O$_3$ nanoparticles are very promising materials for fabricating ethanol sensors (Figure 9).

![Figure 9. Responses of LaFeO$_3$, LaCo$_{0.1}$Fe$_{0.9}$O$_3$, LaCo$_{0.2}$Fe$_{0.8}$O$_3$, and LaCo$_{0.3}$Fe$_{0.7}$O$_3$ nanoparticles to 500 ppm ethanol [116].](image)

Miscellaneous applications of perovskites in solid-state sensors such as infrared, electro-optic, heat, magnetic field, and liquid-state sensors especially in health-care products such as glucose and cholesterol are reported (Table 5). The form of the substrate is thick film including a
nanocomposite of perovskites and a polymer. Typical example of this class is \( \text{La}_{0.67} \text{Sr}_{0.33} \text{MnO}_3 \) (LSMO). A 400 nm thick LSMO films grow on the lucalox (polycrystalline \( \text{Al}_2\text{O}_3 + \text{Mg} \)) substrates via vapor deposition technique. Mechanism of such sensors is based on the change of the film resistivity depending on the applied magnetic field magnitude [119]. Initial resistance and the sensitivity to magnetic field are two important factors depend on ambient temperature. This is a drawback for magnetic field measurements because a temperature compensation mechanism is required. Figure 10 shows a typical magnetic field LSMO sensor. Twisted wires solder to the parts of the electrodes above the substrate (uncovered). Some samples were covered with the polyethylene hot-melt adhesive.

<table>
<thead>
<tr>
<th>Sensing materials</th>
<th>Infrared</th>
<th>Magnetic field</th>
<th>Heat</th>
<th>Electro-optic</th>
<th>Glucose</th>
<th>H(_2\text{O}_2)</th>
<th>Cholesterol</th>
<th>NADH</th>
<th>Acetone</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanate</td>
<td>Ba(<em>{0.25})Sr(</em>{0.75})TiO(_3)</td>
<td>( \text{LaTiO}_3 )</td>
<td>CoFe(_2\text{O}_3)NiFe(_2\text{O}_4)</td>
<td>CoFe(_2\text{O}_3)CoFe(_2\text{O}_4)NiFe(_2\text{O}_4)</td>
<td>Ni(<em>{x})Co(</em>{3-x})Fe(_2\text{O}_4)</td>
<td>[47, 98–100, 118–121]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferrite</td>
<td>( \text{LaTiO}_3 )</td>
<td>( \text{ZnFe}_2\text{O}_4)</td>
<td>CoFe(_2\text{O}_3)CoFe(_2\text{O}_4)NiFe(_2\text{O}_4)</td>
<td>Ni(<em>{x})Co(</em>{3-x})Fe(_2\text{O}_4)</td>
<td>[47, 98–100, 118–121]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mangate</td>
<td>Ni(<em>x)Mn(</em>{3-x})O(_4)</td>
<td>( \text{LaTiO}_3 )</td>
<td>CoFe(_2\text{O}_3)CoFe(_2\text{O}_4)NiFe(_2\text{O}_4)</td>
<td>Ni(<em>{x})Co(</em>{3-x})Fe(_2\text{O}_4)</td>
<td>[47, 98–100, 118–121]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nictate</td>
<td>Li(<em>x)Ni(</em>{2-x})O(_3)</td>
<td>( \text{KTa}_{1-x}\text{Nb}_x\text{O}_3)</td>
<td>CoFe(_2\text{O}_3)CoFe(_2\text{O}_4)NiFe(_2\text{O}_4)</td>
<td>Ni(<em>{x})Co(</em>{3-x})Fe(_2\text{O}_4)</td>
<td>[45, 127]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zirconate</td>
<td>Pb(Zr(<em>{0.52})Ti(</em>{0.48}))O(_3)</td>
<td>KTa(_{1-x}\text{Nb}_x\text{O}_3)</td>
<td>CoFe(_2\text{O}_3)CoFe(_2\text{O}_4)NiFe(_2\text{O}_4)</td>
<td>Ni(<em>{x})Co(</em>{3-x})Fe(_2\text{O}_4)</td>
<td>[10, 128]</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Table 5. Miscellaneous perovskites sensors

Figure 10. Covered and uncovered LSMO sensor (top and cross-section view) [119].
High selectivity, good sensitivity, fast, and reversible response are the main advantages of enzymatic glucose sensors (EGS) [129]. However, some deficiencies prevented wide range applications of EG sensors like the lack of mechanical and thermal stability and also environmental concerns. Development of glucose sensors without using enzymes based on magnetic nanoparticles can play a significant role. The nanoperoxskites can be a good candidate due to the high surface area, high catalytic efficiency, superior mass transport, and strong adsorption ability [120]. Here, an electrode is covered/modified by intelligence perovskite nanomaterials or polymer-perovskite nanocomposite to enhance the sensing properties. In a typical example, polypyrrole is used as shell in polypyrrole–ZnFe₂O₄ magnetic nanocomposites to induce a strict barrier and reduce the magnetic coupling effect between nanoparticles (Figure 11). Electro-oxidation mechanism of glucose on ZnFe₂O₄/PPy core-shell electrode is also shown [121].

![Figure 11](image)

**Figure 11** The illustration of (a) preparation process of modified electrode and (b) electro-oxidation mechanism of glucose on ZnFe₂O₄/PPy core-shell–glassy carbon modified electrode [121].

### 5. Fabrication of gas sensor

Various fabrication techniques have been developed in the production of metal-oxide semiconductor sensors. Purity, porosity, reliability, reproducibility, and expense are the most important factors in selecting the production technique [130]. The mechanism of gas sensors are discussed in previous sections. Thick film and thin film technologies have been popular techniques to miniﬁy various types of the sensors unifying in monolithic hybrid circuits. In the general deﬁnitions, thick ﬁlm depositions are a process of surface modification by applying a thick coating on a substrate. The manufacture of such devices is multilayer coating ﬁlm involving deposition of several layers deposition of conductor, resistor, and dielectric layers on the insulating substrate. Thin ﬁlm technology is a process of deposition of required materials by applying a very thin coating layer often just a few nanometers thickness. Screen printing of ceramic powders, chemical vapor deposition (CVD), sol–gel techniques, spray pyrolysis, physical vapor deposition (PVD), and drop coating [130] are the main techniques for production of metal-oxide films for gas sensors.
5.1. Screen printing

Spiral shape sensing device (screen printing) is one of the simplest sensors in most of the as-reported research articles [13]. Intelligent ink pushes through a porous layer, and it contains the material to be deposited on the substrate. After complete deposition, the print is heated to remove the vehicle, leaving perovskites on the specific target area. Figure 12 indicates a unit of gas sensor containing metal oxide fabricated by screen printing.

![Figure 12. Unit of gas sensor fabricated by screen printing [113].](image)

5.2. Chemical vapor deposition

A heated substrate is exposed to a precursor or controlled mixture of precursors in the vapor phase. The vapors finally interact on the substrate to form a film of the intelligent material. Figure 13 demonstrates a gas sensors fabricated by CVD.

![Figure 13. Gas sensor fabricated by chemical vapor deposition process.](image)

5.3. Sol–gel

A film formation by sol–gel involves the formation of colloidal suspension of solid particles and cross-linking between particles, followed by evaporation, and finally heating the film to form a dense surface on the substrate (Figure 14).
5.4. Spray pyrolysis

The reactants are sprayed on to the target substrate and then react on the surface by continuous heating to form film (Figure 15).

5.5. Physical vapor deposition

The starting materials are transferred into the gas phase by evaporation/sputtering. A reactive gas reacts with the metal vapor, to form a compound, which further deposited on the substrate (Figure 16).

Figure 14. Gas sensing film fabricated via a sol–gel technique.

Figure 15. Schematic representation of spray pyrolysis [131].

Figure 16. Unit of physical vapor deposition.
5.6. Drop coating

Drop coating is a process by where a paste is made of the desired perovskite powder and a solvent; the mixture is then deposited onto a substrate using an appropriate apparatus followed by the evaporation to form a film (Figure 17).

![Figure 17. Drop coating sensor fabrication.](image)

How does a real gas-sensor response to the analyte? The gas-sensor performance measures from the $V_{out}$ of $R_L$ that cascades $R_s$ (the resistance of gas sensor). The resistance of gas sensor ($R_s$) and the sensor response ($S$) obtain from the (Eqs. 6 and 7), respectively;

$$R_s = R_L \frac{V_c - V_{out}}{V_{out}}$$  \hspace{1cm} (6)$$

$$S = \frac{R_s}{R_a}$$  \hspace{1cm} (7)$$

where $R_a$ is the resistance in air and $R_s$ is the resistance in the air mixed with detected gases. The response time is the time required for the conductance to reach 90% of the equilibrium value after a test gas injection, and the recovery time was the time necessary for a sensor to attain a conductance 10% above its original value in air (Figure 18).

![Figure 18. Electrical circuit diagram of a gas sensor [132].](image)
For instance, YCoO$_3$-based sensors (p-type semiconductor) were tested at temperature range of 100–380°C. The obtained response to the gas (here NO$_2$) versus time can be given by the contribution of two different reactions: (a) oxidation and (b) reducing of the surface (Figure 19). The former is faster and favored at low temperature, and the latter is slower and favored at higher temperatures [133].

Artificial olfactory systems (AOS) based on metal-oxides chemiresistors is one of the devices which practically used for sensing the air pollutions. YCoO$_3$ sensors doped with various metals were selected for CO and NO$_2$ detection at different temperatures. At around 280°C, the sensor-doped Pd shows a satisfactory sensitivity with a large response speed to CO gas. The same electrode-doped Co was selected for NO$_2$ pollution sensing. The results clearly indicate that a good sensitivity and a fast response (response time, $T_{10-90\%} = 1$ min, and recovery time, $T_{90-10\%} = 3$ min) at a temperature close to 180 °C [133].

The selectivity toward various target gases such as sulfur dioxide (SO$_2$), ammonia (NH$_3$), hydrogen sulfide (H$_2$S), nitrogen dioxide (NO$_2$) has been discussed before. For instance, 95% sensing response of CoFe$_2$O$_4$ observes toward NO$_2$ compared to other gases at an operating temperature of 150°C, 5 seconds response time and 117 seconds recovery time with NO$_2$ gas [23]. Performing the same sensors for SO$_2$, NH$_3$, and H$_2$S was given just 3%, 6%, and 7%, respectively. The ferrites such as NiFe$_2$O$_4$, ZnFe$_2$O$_4$, MgFe$_2$O$_4$, ZnAl$_2$O$_4$, CoAl$_2$O$_4$, and MgAl$_2$O$_4$ shows the gas response 10–20% for H$_2$S and 1–10% for NH$_3$ gas at 300°C operating temperature.

The sensing response of GaFeO$_3$ toward ethanol vapor at 350°C demonstrates that the resistance declines rapidly in the alcohol atmosphere which exhibited n-type behavior. The response characteristics of the sensors below 350°C for 1 ppm of methanol, ethanol, and isopropanol do not show any significant output. This is due to low thermal energy of the molecules to react with the surface adsorbed oxygen species [105]. Table 6 illustrates some typical experimental results of gas sensing properties of perovskite-based materials.
Table 6. Practical efficiencies of some important perovskites-based sensors.

<table>
<thead>
<tr>
<th>Perovskite</th>
<th>Sensing material</th>
<th>Sensing response (%)</th>
<th>Response time (Sec.)</th>
<th>Recovery time (Sec.)</th>
<th>Response temperature (°C)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCoO$_3$</td>
<td>CO</td>
<td>95</td>
<td>423</td>
<td>377</td>
<td>250</td>
<td>[134]</td>
</tr>
<tr>
<td>AlNbO$_3$</td>
<td>Ethanol</td>
<td>99</td>
<td>24</td>
<td>100</td>
<td>250</td>
<td>[109]</td>
</tr>
<tr>
<td>ZnSnO$_3$</td>
<td>H$_2$</td>
<td>95</td>
<td>1</td>
<td>12</td>
<td>&gt;375</td>
<td>[135]</td>
</tr>
<tr>
<td>ZnWO$_4$</td>
<td>H$_2$O</td>
<td>98</td>
<td>15</td>
<td>158</td>
<td>R.T</td>
<td>[90]</td>
</tr>
<tr>
<td>NiFe$_2$O$_4$</td>
<td>H$_2$S</td>
<td>75</td>
<td>60</td>
<td>300</td>
<td>150</td>
<td>[136]</td>
</tr>
<tr>
<td>CoWO$_4$</td>
<td>NH$_3$</td>
<td>90</td>
<td>3</td>
<td>1</td>
<td>Elevated</td>
<td>[118]</td>
</tr>
<tr>
<td>SmFe$_{1-x}$Co$_x$O$_3$</td>
<td>O$_3$</td>
<td>&lt;80</td>
<td>–</td>
<td>600</td>
<td>R.T</td>
<td>[137]</td>
</tr>
<tr>
<td>La$_{1-x}$Sr$_x$FeO$_3$</td>
<td>CO$_2$</td>
<td>&lt;80</td>
<td>660</td>
<td>300</td>
<td>380</td>
<td>[138]</td>
</tr>
<tr>
<td>LaFeO$_3$</td>
<td>C$_2$H$_6$</td>
<td>93</td>
<td>–</td>
<td>–</td>
<td>250</td>
<td>[139]</td>
</tr>
<tr>
<td>CuFe$_2$O$_4$</td>
<td>LPG</td>
<td>86</td>
<td>5</td>
<td>68</td>
<td>350</td>
<td>[11]</td>
</tr>
<tr>
<td>Zn$_2$SnO$_4$</td>
<td>NO$_2$</td>
<td>–</td>
<td>43</td>
<td>326</td>
<td>200</td>
<td>[79]</td>
</tr>
</tbody>
</table>

6. Summary and recommendation for future research

The oxygen partial pressure dependence of the point defect concentration, and its conductivity, in perovskite semiconductors allows for their application in sensors. The resistance of the aforementioned semiconductors can be affected by other gases, such as O$_2$, CO, NH$_3$, hydrocarbons, and ethanol, which create opportunities for developing new chemical sensors.

In addressing diversity and establishing the current chapter, it is necessary to develop the sensors technology by routine reliable synthesis of self-assembled materials including inorganic materials or inorganic–organic nanocomposites for real-life applications and also commercialization. The need of novel perovskites sensing materials with suitable compositions from all reported perovskites (summarized in Tables 4 and 5) as a filler/cover for sensing device for an especial chemical. The need of high-accuracy sensing device in everyday life especially for health care and also environmental concerns requires a systematic management and researches. For example, a suitable combination of perovskite materials can be identified out of 15 components for ethanol sensors. Moreover, suitable manufacturing technologies, free choice of device geometrical properties to attain the indispensable dimensional efficiencies, optimization of surface for the occurrence of conductance, ease of production flow, and investment expenses are immediately required. It seems that the accurate optimization of perovskite materials applicable in gas sensor is influenced by temperature and partial pressure of oxygen. Therefore, the performance of gas sensor depends on the exact height from the sea level.
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