Review

Oxide and Organic–Inorganic Halide Perovskites with Plasmonics for Optoelectronic and Energy Applications: A Contributive Review

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Abstract: The ascension of halide perovskites as outstanding materials for a wide variety of optoelectronic applications has been reported in recent years. They have shown significant potential for the next generation of photovoltaics in particular, with a power conversion efficiency of 25.6% already achieved. On the other hand, oxide perovskites have a longer history and are considered as key elements in many technological applications; they have been examined in depth and applied in various fields, owing to their exceptional variability in terms of compositions and structures, leading to a large set of unique physical and chemical properties. As of today, a sound correlation between these two important material families is still missing, and this contributive review aims to fill this gap. We report a detailed analysis of the main functions and properties of oxide and organic–inorganic halide perovskite, emphasizing existing relationships amongst the specific performance and the structures.

Keywords: oxide perovskite; metal–halide perovskite; plasmonics; photovoltaics; optoelectronics

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1. Introduction

Materials crystalizing in the perovskite crystal structure are common crystals that are currently employed for multiples applications, including transistors [1], solar cells, light-emitting devices [2], memories [3], catalysts [4], and superconductors [5].

One of the biggest players within the perovskite structures is the family of oxide perovskites. This is a prominent family with the general formula of ABO_3 , where A commonly designates an alkaline or rare earth metal cation, occupying the 12-fold coordinated cuboctahedral cages of the oxygen sub-lattice, and B stands for a transition-metal cation (e.g., Fe, Ni, Mn, Co, Cu, or Ti) coordinated with six oxygen atoms in an octahedral coordination [6].

In fact, in the perovskite structure, distortions frequently occur due to the deviation from ideal values of ionic size ratios between the different A, B, and O sites of the crystal. In addition, A or B cations may have distinctive sizes and valences that could result into oxygen non-stoichiometry, involving both oxygen excess and/or oxygen deficiency.

Perovskite oxides also have high versatility in redox active sites, physico-chemical properties, and oxygen vacancies with controllable compositions, due to several potential substitutions at both A and B sites. For instance, they might be organized either as double perovskite structure of $A_2BB'O_6$ [7,8] or as layered perovskite, depending on their composition or crystal structure. In addition to the composition and the structure, physical and chemical properties are also governed by the perovskite oxides morphology [6,9].

From a historical point of view, the most abundant minerals in the mantle and the crust of our planet are oxides. They constitute minerals with various degrees of structural complexity, ranging from the simplest rock-salt structure to the complex silicates. One of the most dominant families among these minerals is the perovskite structure, which forms a rather simple arrangement but offers an extremely rich variety of cations.

The name “perovskite” was given in honor of the Russian nobleman the Count Lev Alexander Von Perovski (1792–1856), who was a passionate geologist under the Tsar Nicolas

1st era. In 1829, Gustav Rose discovered the first CaTiO_3 perovskite in the Ural Mountains (western Russia). Furthermore, a countless amount of research has been conducted; both ABO_3 oxide perovskites and $\text{A}_2\text{BB}'\text{O}_6$ double perovskites were investigated for more than a century, much before the emanation of halide perovskites.

To cite few typical applications, manganese-based oxide perovskites were dominating for their magnetoresistance property, whereas “cuprates” containing anionic copper complexes have been systematically employed for decades as high-temperature superconducting prototypical systems [10]. Electromagnetic absorption has been efficiently demonstrated using $\text{Bi}_2\text{FeCrO}_6$, and more recently, many studies have been initiated to explore the bulk photovoltaic properties of these oxides; perovskite and the double $\text{Bi}_2\text{FeCrO}_6$ perovskite have demonstrated a power-conversion efficiency up to 8.1% [11–13]. Furthermore, calculations and modeling studies have showed that alloys of $\text{Ba}_2\text{SbV}_{0.25}\text{Ta}_{0.75}\text{O}_6$ oxide double perovskites have a huge potential for solar cell applications [13].

The second pillar of the perovskite family is halide. It has attracted unprecedented interest, from technological as well as scientific perspectives, and even revolutionized the field of emerging photovoltaics within a short period of time [14,15]. In fact, lead-halide PSCs have hit world-record efficiencies above 25.6%, exceeding state-of-the-art thin-film silicon and CIGS technologies [16–18].

Oxides account for roughly 70% of the identified compounds of current perovskites, whereas halides account for just 16% [19]. Surprisingly, there is no particular duplication between these two subclasses, and there is also no direct link between these two areas.

This paper summarizes and reviews inorganic perovskites as well as future expectations. Using nanoparticles that utilize plasmonics effects also highlights the viability of using photon and charge carriers.

Figure 1a displays the recent references related to the oxide perovskite in terms of the distribution of the publications per discipline and applications. Observing Figure 1b, one might notice that the dominating disciplines are physics, material science, chemistry and engineering, with less emergence in other closely related fields such as environmental sciences. This is further evident from Figure 1c, which shows the distribution in terms of application domains; the dominance in the areas of fuel cells, photocatalysis and solar cells is clear.

Figure 1. (a) Latest studies on the oxide perovskite field and their respective distribution of the key words employed and histogram of the type of documents, in the inset. (b) Distribution of the publications per discipline and per (c) applications.

2. Structure of Oxide Perovskite

In the ideal cubic unit cell of a perovskite compound, type “A” atoms are located at the cube corner, at the positions (0, 0, 0), type “B” atoms at the center position (1/2, 1/2, 1/2) and oxygen atoms located at the face positions (1/2, 1/2, 0). Figure 2a shows a ball and stick representation of cubic unit cell where A ions occupy the edges, B ions the center and O ions occupy the faces.

Figure 2. Stick and ball and stick schematic of the (a) ideal cubic perovskite structure unit cell, and (b) a supercell for BaTiO₃ structure.

The relative ion size rules that govern the stability of the ideal cubic structure such as the “Goldsmith tolerance factor” are quite rigid, such that minor buckling and octahedral distortion shall reduce the distorted versions of the symmetry in which the coordination numbers of A, B or both cations are reduced. BO₆ octahedral tilting decreases the coordination of an undersized A cation from 12 to as low as 8. In fact, it helps in attaining a stable bond pattern by removing a small B cation from the center of this octahedron. The resulting electric dipole is the key factor governing the ferroelectricity as shown by perovskites, for example BaTiO₃ (Figure 2b) that distort in this fashion. The most predominant non-cubic variants are the orthorhombic and tetragonal phases. Double perovskites can form upon the incorporation of two distinct B-site cations, forming complex perovskite structures and leading to the formation of ordered and disordered crystal structures.

Complex or mixed oxides are cation groups that contain two or more distinct cations. There are several types of crystal structures. In certain distinctive cases, oxides of a single cation are often known as mixed oxides in different oxidation states.

Perovskite is another significant mixed oxide structure, and many similar oxide structures are known perovskites. The structure of the ilmenite is the same as that of perovskite, i.e., ABO₃, where in this structure, A and B are cations occupying octahedral site of somewhere around the same size; however, the anion packing arrangement is hexagonal and compact in the ilmenite, whereas in the perovskite, the anion and A cation form a close, compact, and a cubic packing structure. Ilmenite has similar stoichiometry to perovskite, but the chemical formula is different. The key difference between ilmenite and perovskite is that ilmenite is an iron-based titanium oxide, i.e., FeTiO₃ mineral, whereas perovskite is a calcium-based titanium oxide, i.e., CaTiO₃ mineral. Moreover, another significant difference between ilmenite and perovskite is that ilmenite is weakly magnetic, whereas perovskite is a non-magnetic material.

In oxide compounds, perovskite oxides have vast families and many perovskite-related structures have been already identified. Large-sized 12-coordinated A-site cations and smaller 6-coordinated B-site cations are standard structures. Wide ranges of oxides and halides, as well as sulfides and perovskites, have a perovskite composition. Because of Therefore, magnesium and iron silicates such as (Mg,Fe)SiO₃ or CaSiO₃ are generally assumed as the geosphere’s primary constituent. Scientists have discovered combinations of different charged cations in sites A and B, such as 1 + 5, 2 + 4 and 3 + 3, relating to

various types of perovskite compounds. Although more complex combinations such as $\text{Pb}(\text{B}'1/2\text{B}''1/2)$ have been found. It is important to keep in mind that B' is always a group containing Sc or Fe, and B'' is always a group containing Nb or Ta. Numerous ABO_3 compounds often crystallize in polymorphic structures that exhibit a slight distortion from the perovskite structure symmetry.

For perovskite, a cubic lattice is the ideal structure and is shown in Figure 2. Numerous oxides have twisted a little with lower symmetries, despite the fact that few compounds have this ideal cubic structure (e.g., hexagonal or orthorhombic). In addition, although the ideal cubic structure of certain compounds may be intact, most oxides feature variants with a lower degree of symmetry. Table 1 lists many examples of perovskite oxides, where the perovskite oxides have mostly grown as rhombohedral lattices.

Table 1. Typical example of perovskite oxides, where the perovskite oxides have mostly grown as rhombohedral lattices.

Compound	Lattice Parameters (Å)		
	a	b	c
A. Cubic Structure			
KTaO ₃	3.989		
NaTaO ₃	3.929		
NaNbO ₃	3.949		
BaMnO ₃	4.040		
BaZrO ₃	4.193		
SrTiO ₃	3.904		
KMnF ₃	4.189		
KFeF ₃	4.121		
B. Tetragonal Structure			
BiAlO ₃	7.61		7.94
PbSnO ₃	7.86		8.13
BaTiO ₃	3.994		4.038
PdTiO ₃	3.899		4.153
TiMnCl ₃	5.02		5.04
C. LaAlO ₃ type			
LaAlO ₃	5.357	$\alpha = 60^\circ 06'$	
LaNiO ₃	5.461	$\alpha = 60^\circ 05'$	
BiFeO ₃	5.632	$\alpha = 60^\circ 06'$	
KNbO ₃	4.016	$\alpha = 60^\circ 06'$	
D. GdFeO ₃ type			
GdFeO ₃	5.346	5.616	7.668
YFeO ₃	5.283	5.592	7.603
NdGaO ₃	5.426	5.502	7.706
CaTiO ₃	5.381	5.443	7.645

A significant characteristic of many compounds is that they often have a wide degree of oxygen or cation deficiencies. The perovskite oxides share the large lattice energy, but due to the large cation and/or oxygen deficiencies, a substantial number of these compounds are nonetheless labeled as perovskite oxides. Ferromagnetism and ferroelectricity are associated forms of distortions within the perovskite structure.

These ABO_3 oxides are strictly termed as ionic crystals for a better understanding of the deviations from the ideal cubic structure. The radii of the A, B, and O_2^- ions in the ideal structure have the following relationship:

$$r_A + r_O = \sqrt{2(r_B + r_O)}$$

Consequently, by using the Goldsmith tolerance factor t , ideal cubic structure deviancy can be determined in perovskite oxides:

$$t = \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}}$$

The t value in perovskite-type compounds is usually between 0.80 and 1.10, i.e., an ideal cubic structure. t values reflect the different polymorphs that exist for perovskite structures. In Figure 3, elements are shown which can be inserted into the perovskite structure are shown. Almost all elements, including dopants, will inhabit the perovskite structure at either A or B positions in the lattice, with the exception of noble gases. In terms of stability and crystal structure, for the A and B cations, ionic radii ratio of is the most significant factor for determining the perovskite structure stability. Structure is not only reliant on the size of the A and B atoms, but also on their chemical composition. For instance, AMnO_3 forms a perovskite structure when the A cation is La or Ce–Dy, and forms a hexagonal structure when A = Ho–Lu or Y if A = La or Ce–Dy with 5- and 7-coordination of Mn and A, respectively [17].

Figure 3. (Upper panel) In the perovskite structure, the B-site cation can be taken by chemical elements. (Lower panel) Representation of the oxide family (left), halides (right), single (top), and double (below) perovskites, and other analogs.

At this site, the primary emphasis should be on the B atom's nature, where the covalent bond nature causes a coordination number of 6, which is rather low. The structure of BaGeO₃ is an example of this kind. Although the ideal ionic size combination of BaGeO₃ results in a *t* value near to 1, which implies the perovskite structure, BaGeO₃ instead crystallizes in the silicate-related structure. The coordination number of Ge is four, which can be attributed to this. On the other hand, new Ge-based perovskite oxides have been identified from the developments in high-pressure technology [18]. By increasing the pressure, the Ge coordination number increases, and this higher coordination number is favorable for the formation of the perovskite structure, e.g., CaGeO₃. Oxynitrides are another perovskite compounds group, i.e., LaWO_{3-x}N_x, LaTaO₂N, etc. As a result, the ionic size which is dependent on the tolerance factor value *t*, is an important index for perovskite structure stability. However, the coordinating number contribution of the constituent elements must also be considered.

Next, superstructure formations in perovskites are discussed. Progressive substitution of the B-site cation by a dopant contributes to a significant difference in the ionic radii, and this can be conducive to the formation of the superstructures. Ba₂CaWO₆, also known as Ba₂(CaW)O₆, is a clear example of this. Analogously, when M is Fe, Co, Ni, Zn, or Ca, there is a random distribution of M and Ta ions in the octahedral positions in the compounds with the general formula Ba₃MTa₂O₉, whereas Ba₃SrTa₂O₉ forms a hexagonal lattice superstructure. On A sites, the cation vacancy ordering, as seen in MNb₃O₉ (M = La, Ce, Pr, Nb) and MTa₃O₉ (M = La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Y, Er), is another interesting form of superstructure observed in perovskites. Often known as the Brownmillerite (A₂B₂O₅) and K₂NiF₄ structures, the perovskite polymorphs contain these two. The low-oxygen-deficiency type of perovskite, where oxygen vacancies are ordered, is known as Brownmillerite (A₂B₂O₅).

In an ordered arrangement, the unit cell comprises BO₆ and BO₄. The A-site cation coordination number is reduced to eight due to the oxygen deficiency. For an ideal perovskite, the cubic lattice parameter (*a_p*) is associated with the lattice parameter of Brownmillerite structure:

$$a = b = \sqrt{2a_p}c = 4a_p$$

Due to the large number of oxygen defects, Cu-based oxides and Ni-based oxides both develop oxygen-deficient structures. For exhibiting superconducting properties, K₂NiF₄ structures are well known and are found to be combined with ordered B-sites and oxygen defects.

Two units, namely the KNiF₃ perovskite unit and the KF rock salt unit, are linked in series along the *c* axis to form K₂NiF₄ structures. K₂NiF₄ is entrenched in the *c*-axis direction, and it has strong two-dimensional properties. There are several structures known as Ruddelsden–Popper compounds with the general formula (ABO₃)_nAO (see Figure 4), such as Sr₃Ti₂O₇ (*n* = 2) and Sr₄Ti₃O₁₀ (*n* = 3), based on the intergrowth of different numbers of KNiF₃ and KF units [19]. The isostructural Sr₂TiO₄ or Ca₂MnO₄ can be contrasted with SrTiO₃ or CaMnO₃, which crystallize in perovskite structures. It is also possible to shape the perovskite and rock salt units with two separate A cations: an example of this is LaO._nSrFeO₃. An even more significantly modified version of K₂NiF₄ is where the two separate anions exclusively occupy the two building blocks, i.e., SrFeO₃.SrF or KNbO₃.KF. For any scenario, it is obvious that these structures are complex compounds. As a result, these compounds are supposed to possess various crystal properties and characteristics [20–22].

Figure 4. Another perovskite-related structure is the Ruddlesden Popper structure.

The layered perovskite family contains several polar and ferroelectric materials in contrast to bulk ABO_3 perovskites. The (100)-oriented 2D perovskites are by far the most abundant class, and have been explored for a wide variety of cation templates. The geometrically planar inorganic–organic interface of the (100)-oriented layers not only allows the incorporation of a plethora of “spacer” cations between the 2D perovskites, but it also allows for the template “build-up” of the perovskite itself, which self-assembles in a layer-by-layer fashion between the spacers. These modular multilayered structures were first discovered in the oxide perovskites, where they were used to expand extended homologous series [19,23]. Following the oxide perovskite nomenclature, the (100)-oriented oxide perovskites can be further categorized as the Ruddlesden Popper (RP) phases [24,25], the Dion Jacobson (DJ) phases [24,25], and the Aurivillius phases [26,27], as shown in Figure 5, [28] where their general formulae can be written as $\text{A}'_2\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}$, $\text{A}'\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}$ and $(\text{Bi}_2\text{O}_2)(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})$, respectively.

In the case of halide perovskites, most of these structure types have been realized, with the exception of the Aurivillius phases. It is entirely possible, however, that such layers can be formed using less reactive rock-salt-type layers, such as $(\text{Ba}_2\text{F}_2)^{2+}$. As in the case of oxide perovskites, as well as in the case of halide perovskites, the nature of the spacer cation is important. Already, from the expression of the chemical formula, it is evident that the charge of the spacer cation defines the structural types of 2D perovskites. Nevertheless, both RP and DJ classes exist for the halide family, having the general formula of $\text{A}'_2\text{A}_{n-1}\text{B}_n\text{X}_{3n+1}$ and $\text{A}'\text{A}_{n-1}\text{B}_n\text{X}_{3n+1}$ (A' = interlayer “spacer” cation).

Figure 5. Layered perovskites—derived from the cubic ABO_3 aristotype—are discussed in this perspective. In the Dion Jacobson phases, A' is usually an alkali cation, but can also be a transition metal–halide complex, e.g., $(MnCl)^+$. In the A-site ordered double perovskites, A' is chemically different from A . The perovskite blocks are interleaved between $[Bi_2O_2]^{2+}$ layers in the Aurivillius phases. Adapted from Refs. [26,27] with permission from the European Society for Photobiology, the European Photochemistry Association, and The Royal Society of Chemistry.

3. Formability versus Thermodynamic Stability

Recently, Talapatra et al. [29] studied the relationship between two key properties governing the stability of single and double perovskites. The formability stands for the practical ability to synthesize a compound, whereas the thermodynamic stability stands for the thermodynamic preference to form a given structure or polymorph among several other possible crystal structures. The data set contains information from the literature which have been reported from experimental research as well as from DFT calculations. It consisted of 1505 simple oxide perovskites ABO_3 and 3469 double-oxide perovskites $A_2B'BO_6$, $AA'B_2O_6$ and $AA'BB'O_6$, sampling a limited chemical space within the periodic table. They subsequently built machine learning classification models to screen and identify novel stable oxide perovskites. One of the most important finding is that they succeeded to make a clear difference between the perovskite's formability and the thermodynamic stability and to relate these two stability measures to the elemental properties of constituent chemical elements.

The formability of perovskites relies on geometrical consideration based on the ionic radii of the perovskites as well details in the sections above. However, this formability metric, although popular, does not inform us on whether the perovskite structure is the most favorable compared to other possible crystal structure, here is where the importance of thermodynamic stability arises. Under certain conditions, including temperature, pressure or variation in chemical potentials, some other crystal structures of polymorphs might be more stable than the perovskite one, even if they are favorably formable. The distance from the convex hull, also called ΔE_h , might be a better thermodynamic stability measurement. Authors [29] have used the threshold of $\Delta E_h \leq 50$ meV as the limit that defines the cubic thermodynamic stability of the oxide perovskite, which is a value that is highly accepted by the community [30,31]. Using a random forest classification algorithm, Talapatra et al. [29] determined the most elemental features governing both stability metric and generated a very good accuracy predictive model for both stability metrics. Figure 6a shows an interesting finding within a plot of the energy above the hull as a function of the geometrical tolerance factor for the groups of materials that fulfill both the formability and stability criteria. One might notice that below the $\Delta E_h = 50$ meV, dashed line lies a high population of perovskite material (66%), whereas the prevalence on non-perovskites is rather rare. Nevertheless, a non-negligible fraction of the compounds was excluded from the thermodynamic stability because of their high energy above the

hull. Taking $\Delta E_h < 400$ meV as a threshold appears to give more reliable classifications of the compounds, as also demonstrated from the histogram of incidence (frequency) of perovskites and non-perovskites within ΔE_h bins of 50 meV each. The histogram indicates that up to $\Delta E_h = 400$ meV compounds crystallizing in the perovskite structure are dominant, as shown in Figure 6b.

Figure 6. (a,b) Energy above hull (ΔE_h) in meV as a function of tolerance factor (t) for candidate materials identified as stable and formable. Reproduced with permission from Ref. [29].

Hence, the cubic thermodynamic threshold of $\Delta E_h \leq 50$ meV might not be a reliable threshold for the metastability of oxide perovskite because it does account for stability enhancements due to octahedral tilts and octahedral deformation and elongations. It is concluded that the thermodynamic cubic stability must be selected carefully and should be tuned properly to include lower symmetry phases as well. This study and previous studies constitute very interesting advances in the prediction of novel oxide perovskites for targeted applications while taking into account their stability and formability prior to recommending their experimental synthesis in the laboratory.

4. Typical Properties of Perovskite Oxides

Perovskite oxides have a diverse plethora of properties because of their different compositions and structures. In BaTiO_3 -based oxides, and in $\text{Ba}_2\text{YCu}_3\text{O}_7$, perovskite oxides exhibit ferroelectricity and superconductivity, respectively. Several perovskite oxides also exhibit substantially greater electric conductivity, ionic conductivity, and mixed ionic conductivity than many metals. For use in solid oxide fuel cells (SOFC), perovskite oxides have been preferred, with components based on differences in electrical conduction [32]. Table 2 lists the properties of several common perovskite oxides. Perovskite oxides take on several feature properties, such as ferroelectricity, magnetism, superconductivity, and catalysis.

Table 2. Typical perovskite oxide properties.

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

4.1. Dielectric Properties

Ferroelectricity, piezoelectricity, electrostrictivity, and pyroelectricity, which are important electroceramic characteristics, are special properties of dielectric materials. BaTiO₃, PdZrO₃, and their doped compounds are all well known for their ferroelectricity. It has been investigated in depth that there is a close correlation between the ferroelectric activity of BaTiO₃ and its crystal structure. BaTiO₃ can be present in three distinct phases: monoclinic, tetragonal, and cubic. The transition between the phases occurs with a rise in temperature. As a matter of fact, above 303 K, cubic BaTiO₃ is obtained, which is non-ferroelectric in nature. Crystal structure anisotropy may explain BaTiO₃'s high dielectric constant.

4.2. Electrical Conductivity and Superconductivity

The superconductivity of perovskite oxides is the most famous characteristic among the other features. In La–Ba–Cu–O perovskite oxide, superconductivity was found and introduced for the first time by Bednorz and Müller in 1984 [33]. After their report, much attention was drawn towards high-temperature superconductors, particularly Cu-based oxides, which were given much attention after their report. Other than Cu-based oxides, data have been reported on numerous superconducting oxides with different A-site cations. On the B-site, Cu presence is crucial for superconductance, however. YBa₂Cu₃O₇ system [33] and Bi₂Sr₂Ca₂Cu₃O₁₀ system [34] superconductors were reported in 1987 and 1988, respectively. The critical temperature of the superconducting transition (T_c) in the HgBa₂Ca₂Cu₃O_{8+δ} system has been further increased to 130–155 K [33]. All superconducting oxides at high temperatures are cuprites; therefore, superconductivity is specifically correlated with the layers of copper oxide, as well as the T_c (critical superconductivity temperature), and the values are summarized in Table 3:

Table 3. Superconductivity correlated with the number of Cu–O layers.

Number of Layers	T_c (K)
1	30
2	90
3	110
4	120

A further rise in Cu–O layer numbers is predicted to contribute to higher T_c values. Five or more copper oxides layers have not been effective until now due to the low chemical stability. YBa₂Cu₃O₇ is amongst the most significant high- T_c superconductor systems, and extensive studies have been already carried out on its crystal structure. In addition, the nonstoichiometric oxygen content is a key factor in high T_c . If the δ value is less than 0.5,

$\text{YBa}_2\text{Cu}_3\text{O}_7$ crystalizes in a superconductive orthorhombic structure, whereas for $d > 0.5$, it is tetragonal structure, which is non-superconducting.

In addition to the superconductivity, there are numerous perovskite oxides with a high electronic conductivity, even close to that of metals such as Cu. LaCoO_3 and LaFeO_3 are the most common examples of perovskite oxides, whereas LaMnO_3 is now widely used in SOFCs as a cathode. Superior hole conductivity as high as $\sigma = 100 \text{ S/cm}$ is exhibited by these perovskite oxides, which is attributed to the excess oxygen [35,36]. Doping at the aliovalent cation site also leads to considerably improve the electrical conductivity, because the charge compensation creates an increased number of mobile charge carriers.

4.3. Catalytic Activity

Perovskite oxides have been investigated in depth as catalysts for different reactions, due to the diversity of components and their high chemical stability. Two types of research-trends are indicated on this front. The first one is related to develop catalysts for oxidation as a substitute to the precious metals catalysts, or oxygen-activated catalysts. The second one is to consider the perovskite as an active site platform. The stable nature of perovskite enables compounds to be prepared with an exceptional element of valences or with an enhanced degree of oxygen deficiency. It has been reported that perovskite oxides provide a high catalytic activity because there are a lot of oxygen vacancies, and it also depends -although partly- on the high surface activity to reduce oxygen or to activate it. From the examination of different catalytic reactions, environmental catalysis has gained a special attention (e.g., catalysts for the exhaust gas cleaning of automobiles). Initially, perovskite oxides, comprising Fe, Cu, Mn or Co, were known to increase activity at higher temperatures than that obtained from a direct NO decomposition [37–39]. The process related to $2\text{NO} = \text{N}_2 + \text{O}_2$, where a direct NO decomposition takes place, is an ideal reaction in the catalysis. Easy separation of oxygen at the surface as a reaction product has a vital role because perovskite oxides are active due to oxygen deficiency at high temperatures. Doping is noted to be highly successful in enhancing the NO decomposition operations. It has been identified that the perovskite $\text{Ba}(\text{La})\text{Mn}(\text{Mg})\text{O}_3$, in a rich environment of oxygen, can obtain a fairly high NO decomposition rate (up to 5%) [38–40].

Perovskite oxides are also used as catalysts for automobiles for the self-regeneration of precious metals in a usage ambience without auxiliary treatment [41,42]. To date, for the removal of NO, CO and non-combusted hydrocarbons, three-way catalysts (TWC) and Pd–Rh–Pt catalysts have been used widely. The fine particle catalyst with a high volume-to-surface ratio must lower the needed quantity of precious metals. Even then, they are not stable under operational circumstances and can sinter easily, and the catalyst is therefore deactivated. The redox properties of perovskite oxides were suggested in order to preserve a high degree of dispersion, i.e., palladium is oxidized under oxidation conditions and stays as $\text{LaFe}_{0.57}\text{Co}_{0.38}\text{Pd}_{0.05}\text{O}_3$ where palladium nanoparticles (1–3 nm) are deposited under reduced conditions. Such oxidation and reduction of the catalyst lead to partial Pd substitution and deposition from the perovskite base, thereby retaining a high degree of Pd dispersion. This was considered to be significantly successful in enhancing long-term Pd stability while removing NO_x , CO and hydrocarbons from the gas exhausted. By displaying the catalyst in oxidation and reduction environments, high-dispersion status Pd can be restored. Therefore, this catalyst is often termed as an intelligent catalyst. Such character is attributed to the perovskite crystal structure stability. In the lattice, the redox couples of another cation naturally accommodate for the charge. Photocatalysts for water splitting are another important application of perovskite oxides. The use of ultraviolet light among catalysts for water splitting into H_2 and O_2 is observed to have an increased activity of perovskite oxide based on Ta and Na.

4.4. Photocatalytic Activity

It is possible to use photo-excited electrons and holes to split H_2O into H_2 and O_2 , and this process gains more attention in solar energy conversion into hydrogen. Several

inorganic catalysts for water splitting have been investigated as water photocatalysts, especially Pt/TiO₂ as a well-known photocatalytic inorganic semiconductor. In the photocatalytic water-splitting reaction, the Ta-based oxide is normally active. The Ta-based perovskite oxide, ATaO₃ (A = alkaline cation), specifically displays high water-splitting activity [43]. The A cation strongly affects the activity because the crystal structure is linked to the oxide's electronic configuration. The Ta–O–Ta bond angles are 143° (LiTaO₃), 163° (NaTaO₃), and 180° (KTaO₃). The bonding angle close to 180° means that excited energy migration easily occurs in the crystal and results in a smaller band gap. Hence, LiTaO₃ < NaTaO₃ < KTaO₃ is the delocalization order of excited energy and vice versa for these band gaps, as shown in Figure 7. Table 4 presents the photocatalytic water-splitting activities of pure water into H₂ and O₂ on alkaline tantalite photocatalysts with and without NiO cocatalysts. When NiO cocatalysts were loaded, NaTaO₃ photocatalysts demonstrated the highest photocatalytic activity. In this case, excessive amounts of Na in the starting material were necessary to demonstrate high activity. The photocatalyst NaTaO₃'s conduction band level was higher than the NiO level (−0.96 eV), as shown in Figure 7 [43]. In addition, in the NaTaO₃ crystal, the excited energy was delocalized. Therefore, the photogenerated electrons in the NaTaO₃ photocatalyst's conductive band were capable of passing to the NiO cocatalyst's conduction band of an active site for H₂ generation, leading to an increase in the separation of the charge. Hence, even without special pretreatment, NiO loads were successful for the NaTaO₃ photocatalyst.

Figure 7. Band diagram of a hydrogen electrode-based alkali tantalates ATaO₃ (A = W Li, Na, and K) band structures with perovskite-type structures. Adapted from Ref. [43].

Table 4. Appropriate perovskite oxide materials for use in SOFCs.

Component	Typical Materials
Interconnector	La(Ca)CrO ₃
Anode	SrTiO ₃ , La _{1-x} Sr _x Cr _{1-y} M _y O ₃ (M = Mn, Fe, Co, Ni),
Electrolyte	La(Sr)Ga(Mg)O ₃ (O ²⁻), SrZrO ₃ (H ⁺), Ba ₂ In ₂ O ₅ (O ²⁻), BaCeO ₃ (H ⁺), BaZrO ₃ (H ⁺),
Cathode	La(Sr)Fe(Co)O ₃ , La(Sr)CoO ₃ , La(Sr)MnO ₃ , Sm _{0.5} Sr _{0.5} CoO ₃

5. Multiferroic Oxide Thin Films

Multiferroics jargon applies to materials where two or more ferroelectric orders coexist, such as anti-ferromagnetism, ferroelectricity, and ferroelasticity. Between ferroic orders, strong coupling can yield substantial features, particularly magnetoelectric effects, which also allow an electric field to control electric polarization by a magnetic field as well as its magnetization. It is a consequence of great achievements in physics and science behind the various new fields of multifunctional computers and memory [44–47].

5.1. Synthesis of Multiferroic Thin Films and Strain Engineering

An undeniable fact is that the development of tools used to deposit thin multiferroic films has been empowered because of the breakthroughs in thin film deposition techniques [48,49]. In contrast to the conventional approaches, the characteristics of thin multiferroic films could be improved with the proper optimization of the synthesis parameters.

In the 1960s, for instance, BFO was investigated thoroughly. However, due to the leakage problems linked to its poor crystal quality, its spontaneous polarization yielded only a few $\mu\text{C}/\text{cm}^2$ [50–52]. This dilemma was finally resolved by quality thin-film growth in 2003, and was one of the landmarks in the multiferroics field with the use of pulsed laser deposition (PLD) [53].

Efficient thin-film growth is the starting point and the cornerstone of the innovation and development of most electronic devices, but it brings many complicating factors such as the strain in the substrate, surface conditions, degree of impurities, structure imperfections, etc. Too much leakage current, for instance, may affect the ferroelectricity measurement; in addition, spin canting can be incorporated due to the surfaces and interfaces and consequently affects the magnetism. Therefore, it is essential that techniques for keeping or enhancing thin multiferroic films properties are secured.

To fabricate multiferroic thin films, various SOTA physical deposition techniques have been used, such as PLD, sputtering and molecular beam epitaxy (MBE) as well as in chemical deposition paths, such as sol–gel, metal–organic chemical vapor deposition (MOCVD), and spin coating. PLD is the most commonly applied technique by researchers, especially for the investigation of new materials and heterostructures. PLD's inherent benefit is that the growth process occurs far from optimum; therefore, it is capable of maintaining complicated stoichiometry, which is necessary for multi-element compound growth. In addition, PLD, which is equipped with high-energy electron diffraction (RHEED) reflecting on-site, facilitates efficient film thickness control at the level of the unit cell [53], which is essential for enhanced epitaxial thin films synthesis. Unlike MBE, PLD requires very low energy (~ 1 eV) thermal atomic beam generation, which is appropriate for highly perfect thin multiferroic film fabrication as well as other complex oxides [53]. PLD and MBE can fabricate superior quality films, but they are costly when applying for mass production. For mass production, sputtering techniques are extensively used, namely, magnetron sputtering, ion-beam sputtering, and off-axis sputtering [54]. For the fabrication of high-grade thin oxide films with the required stoichiometry of oxygen, accurate reactive gas control, in particular O_2 or Ar/O_2 mixtures, is essential. For thin-film fabrication on large areas with low costs, sol–gel spin-coating is also an appropriate and cost-effective chemical process.

The films obtained are, therefore, mostly in polycrystal or textured structures, and the sample thicknesses and morphologies are challenging to tweak. Consequently, in the electronics industry, MOCVD has commonly been used, providing remarkable prospects for multiferroic film deposition owing to multiple features, including outstanding film homogeneity throughout large areas, significantly higher deposition rates, and compliance with current integrated circuit technologies [55]. However, limited metal–organic sources of complex oxides are available. In a few recent articles, more knowledge on the growth of thin films with ferroelectric and multiferroic oxides can be extracted [56–58].

5.2. Bi-Containing Multiferroic Thin Films

(i). BiFeO_3

One of the most promising stories in the field of multiferroic research is BiFeO_3 , which demonstrates ferroelectric and magnetic room temperature orders ($T_C = 830$ °C and $T_N = 370$ °C). The development of ferroelectric polarization is motivated by more polarizable Bi lone pair ordering, whereas in adjacent Fe and O ions, super-exchange contributes to the antiferromagnetic order of the G-type. With lattice parameters of $a_{\text{hex}} = 5.58$ Å and $c_{\text{hex}} = 13.90$ Å, bulk BFO is a rhombohedral (space group: $R3c$), whereas a lattice parameter $a = 3.965$ Å is for its perovskite-type unit cell [59,60].

(ii). BiMnO₃ (BMO)

BMO is a distinctive multiferroic material of a ferromagnetic ($T_{\text{FM}} = 105$ K) and a ferroelectric ($T_{\text{FE}} = 770$ K) ground state with simultaneous polarization ($P \sim 16$ $\mu\text{C}/\text{cm}^2$) and magnetization ($M \sim 3.6$ $\mu\text{B}/\text{Mn}$) [61]. Similarly to BFO, the ferroelectric state in BMO is activated by the stereochemical behavior of the lone pairs of Bi 6 s^2 , whereas the ferromagnetism emanates from the ferromagnetic superexchange interplay between Mn^{3+} ions. For bulk BMO single-crystal synthesis, high pressure is needed; however, epitaxial stability in thin films may solve this challenge [62]. Its magnetic property is highly sensitive to growing parameters related to the Bi vacancy and the substrate strain effect [62–64].

(iii). BiCrO₃ (BCO)

In contrast to BFO, there are fewer researched data sets available for BCO thin films [65–67]. In BCO, a G-type antiferromagnetic ground state with distortion of the antiferroelectric structure was first hypothetically presumed by Hill [65]. Piezoelectric behavior and controllable dielectric constant were confirmed by Murakami et al. [67] in an epitaxial BCO thin film developed on the LaAlO_3 (LAO) substrate where weak ferromagnetism occurs at low temperatures. Another characteristic perovskite multiferroic material is BCO, with a large A-site Bi_3p , where antiferroelectricity and poor parasitic ferromagnetism have been shown [67,68].

(iv). Bi-Based Ordered Double Perovskites

Perovskites such as $\text{BiFe}_{0.5}\text{Mn}_{0.5}\text{O}_3$ and $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ are known as ordered double perovskites. These are Bi-based transition metal perovskites, i.e., BiMO_3 , where $M = \text{Fe}, \text{Mn}, \text{Cr}$, etc., were hypothesized to be intriguing materials with multiferroic properties for which significant spontaneous polarization and ferromagnetism could subsequently be experienced [56,65].

5.3. Multiferroic Rare-Earth Manganites

Rare-earth (RE) manganites are a fascinating class of compounds that seem to have a hexagonal structure if the R ionic radius is small ($P6_3cm$, from Sc, Y, and Ho to Lu), or if the ions are large, an orthorhombic structure ($Pnma$, from Dy to La). Around Y/Ho, the overlap is shown in Figure 8 [69]. The latest investigations have shown that hexagonal manganites carrying a small ionic radius R can be converted into the orthorhombic phase using thin-film growth, high-pressure treatment, or soft chemical synthesis. Interesting physical properties have been revealed in the subsequently obtained orthorhombic phases. Conversely, by leveraging the epitaxial strain, the subsequently formed phase can also be converted back, and the related physical properties can be changed accordingly [70–72].

Figure 8. Evolution of the lattice structure in REMnO_3 as a function of the size of the rare-earth (RE) element. Reprinted from Ref. [57].

(i). Antiferromagnetic REMnO_3

Throughout the alternatively packed c axis, YMnO_3 (YMO) with MnO_5 trigonal bipyramids (distinct from MnO_6 octahedrons in the perovskites) and Y3p are the most investigated hexagonal REMnO_3 . $A = 6 \text{ \AA}$ [11], and $c = 11 \text{ \AA}$ [4], are the lattice parameters of YMO [58]. YMO's noticeable added benefit is that it comprises no volatile elements, such as Bi and Pb. Therefore, due to the geometric constraint, hexagonal YMO spin configuration is hindered. By robust in-plane antiferromagnetic super-exchange interaction, the spins of Mn^{3+} are controlled in the MnO_5 bipyramid layers (ab plane) and confined within the plane.

(ii). Orthorhombic REMnO_3 with Spiral Spin Order (SSO)

In 2003, Kimura et al. [73] in 2003 were the first to report magnetic ferroelectricity regulations in TMO. Having $a = 5.2931 \text{ \AA}$, $b = 5.8384 \text{ \AA}$, and $c = 7.4025 \text{ \AA}$ as lattice parameters, TMO has a perovskite crystal structure [69]. The breaking of spatial-inversion and time-reversal symmetries works synergistically in this material, and the intrinsic magnetic structure, i.e., SSO, produces ferroelectricity. Tens of magnetically activated multiferroic materials have been formulated so far, and two forms of SSO have been shown to be essential for spontaneous polarization production [74,75].

5.4. Other Multiferroic Thin Films

The exploration for further high-performance multiferroic materials has been productive. One observation is provided here, i.e., CuMO_2 ($M = \text{Cr, Mn, Fe, or Co}$) delafossite-type. The two-dimensional (2D) triangular crystal structure of this class of materials has M oxide magnetic layers and the cuprous oxide layers packed along the c axis. Due to the intrinsic multiferroicity induced by the frustrated spin configuration, these 2D triangular antiferromagnets have attracted a great deal of attention [76,77]. For CuCrO_2 , it was shown that the reversal of ferroelectric polarization could be precisely adjusted via electric and magnetic fields [78]. Multiferroic CuMO_2 thin films have been identified, and UV-Vis-NIR measurements have been performed on these thin multiferroic films [79,80].

5.5. Magnetism in Multiferroic Thin Films

In most well-studied multiferroic materials such as BFO and TMO, the antiferromagnetic spin order coexisting with ferroelectricity does not contribute significantly to any macroscopic magnetic moment. Canting by the Dzyaloshinskii–Moriya interaction (DMI) of the AFM-aligned spins will lead to weak FM [81]. It is advantageous for applications involving multiferroic devices to improve the magnetism of these materials and to obtain significant purposeful magnetism. There are numerous published mechanisms in the literature for increasing magnetism in multiferroic oxide thin films. Most of the work in this regard has been performed on BFO. Holcomb et al. [82] found that the antiferromagnetic process in epitaxial BFO thin films is susceptible to strain and thickness, by integrating temperature- and angle-dependent dichroic measurements and spectroscopy. In thin films of $\text{BFO}/\text{LaAlO}_3$ with strong compressive strain, where the saturated magnetism and coercivity of the highly strained phase are approximately six times greater than those of the relaxed phase, analogous magnetic modulation has been found [70]. $\text{BFO}/\text{LaAlO}_3$ thin films have shown a small but definite spin glass (SG) transition [70,83]. Proportionally, strain may have a significant impact on the magnetic properties of BFO thin films. It is noticeable that for integration into functional devices, glassy magnetism would not be too strong in thin BFO films.

6. Photovoltaic Effect in Multiferroic Thin Films as a Photoactive Layer

In recent years, fascinating PV effects have been observed in thin films of BFO with patterned domains, due to which the resulting voltage is considerably larger than the bandgap (Figure 9) [84,85]. A ferroelectric-domain-based model has been proposed in attempt to elucidate this novel PV effect in BFO thin films [85,86]. The developed potential

steps triggered by the polarization component will efficiently separate photo-generated electrons and holes. An overall electrical voltage across the sample would be produced by the aggregation of electrons/holes in the domain walls, possibly contributing to the observed open circuit photovoltage.

Figure 9. (a) Walls periodic arrays PFM image (71° domain). (b) Schematic of the X-ray rocking curves along two orthogonal crystal axes are shown in the inset. Arrows indicate the ferroelectric polarization of different components. Representative illustrations of domain walls parallel (c) at (d) at right angles. The responsive measured I-V curves are perpendicular to the domain walls (e) and parallel to the domain walls (f). Reproduced with permission from Ref. [87].

PV effects without striped domains and even in bulk single-crystal monodomain were observed in BFO thin films by many groups [62–64,71,87]. Furthermore, without a regular domain configuration in conventional ferroelectrics, PV effect has also been detected [88–90]. Bhatnagar et al. conducted temperature-dependent PV effect measurements in BFO thin films with regard to the site of domain walls on the abnormal PV effect, and demonstrated that the bulk PV effect is the root cause [91], and showed a significant lasting PV effect in a strained BFO [72]. Yuan et al. [92] suggested a model to describe the PV effects in ferroelectric materials wherein the depletion region is altered by switching the polarization, after comparison with the typical PV effects in p-n/Schottky junctions, so that the polarization PV current and voltage directional dependence can be adjusted. The bulk photovoltaic effect is usually observed to be switchable with the reversal of polarization [87], which is implied to be due to the transition caused by the polarization between Ohmic and Schottky contacts and the defects of electromigration such as vacancies of oxygen [93]. Based on this concept, Guo et al. recently suggested a new type of non-destructive

FeRAM device [94]. The fundamental concept is to use the short circuit current (I_{sc}) or the open circuit voltage (V_{oc}) to determine the polarization direction. The model device structure, where a positive (negative) V_{oc} refers to the up (down) polarization, is shown in Figure 9. When the device is illuminated with light, both V_{oc} and the polarization state can be read.

Kundys et al. [95] recently reported a fascinating phenomenon with respect to the light-induced effect: by the illumination of light, the size of the BFO crystal can be controlled. Photostriction observations suggest the possibility of understanding mechanical, magnetic, electrical, and optical functionalities in monolithic multifunctional devices.

7. Oxygen-Separating Membrane

Perovskite oxides demonstrate electronic and oxide ionic conductivity of a greater degree, known as mixed conductors. Electronic conductivity in these, such as ion transfer, can be obtained naturally, because in mixed conductors, ions can be transferred without external circuits. Therefore, one of the useful applications of these mixed conductors is the oxygen-separation membrane.

Diffusivity for oxide ions is displayed in Figure 10 for typical perovskite oxides that can be used for oxygen permeation membranes [96,97]. It is reported that high oxide ion conductivity has been observed by Fe- or Co-based perovskite oxides. Therefore, it is predicted that their oxide ion permeability is high. The oxygen permeation rate is 1:05 mL/cm² min at 1173 K of Ba_{0.5}Sr_{0.5}Fe_{0.8}Co_{0.2}O₃ (BSCF) (2 mm thickness) [97]. Across the membranes, identical oxygen partial pressure gaps appear; then, using the ion diffusivity and membrane thickness, the oxygen permeation rate can be calculated. As a result, as the membrane thickness decreases, the oxygen permeation rate should increase; however, the oxygen permeation rate is dependent on the membrane thickness when the thickness is high. However, as thickness decreases, the oxygen permeation rate becomes independent of membrane thickness due to surface reactions of oxygen dissociation. This means that when a high diffusivity of oxide ions in the bulk is needed, oxygen dissociation surface activity must also be high. The new uses for perovskite-related oxides make them very common for mixed conductors, and their applications for oxygen permeation membranes are also growing. There is a high interest in K₂NiF₄-type oxides in perovskite-related oxides due to their high oxygen deficiency. Thus, the ideal application might be the perfect blend of mixed conductors and catalytic reactions.

Figure 10. Diffusivity of oxygen ions in various perovskite oxides employed in an oxygen permeation membrane. D^* , D_v calculated from the tracer diffusion coefficient; D_{chem} , D_v calculated from the chemical diffusion coefficient. Adapted from Ref. [97].

For the separation of oxygen from the air, partial oxidation of CH_4 was investigated with mixed perovskite conductors [98]. Partial oxygen pressure in CH_4 is as low as 10^{-20} atm.; therefore, a high rate of oxygen permeation is obtained within partial CH_4 oxidation conditions, and it has been stated, using $\text{SrFe}_{0.8}\text{Co}_{0.2}\text{O}_3$ perovskite, that the oxygen permeation rate is 5 cc/min cm^2 [99]. In a reducing atmosphere of CH_4 , however, phase transitions minimize the oxygen permeation rate. Although Fe- or Co-based perovskites have primarily been studied, stability within a broad oxygen partial pressure range is the major problems with the application of perovskite oxides on catalytic membrane reactors, and it has been stated that Ni- or Fe-doped LaGaO_3 exhibits a stable hole and oxide ion conductivity over a broad $p\text{O}_2$ range, with an oxygen permeation rate of 12 cc per min on $\text{La}_{0.7}\text{Sr}_{0.3}\text{Ga}_{0.6}\text{Fe}_{0.4}\text{O}_3$ of 0.2 mm thickness at 1273 K in CH_4 partial oxidation [100]. Oxygen separation membranes and the application of catalytic membrane reactors both have significant uses, but there is a vital necessity for enhanced chemical stability.

8. Perovskite Oxides for Solid Oxide Fuel Cells (SOFCs)

Due to the high oxygen-reducing catalytic activity and outstanding mixed conductivity at the same time, SOFCs and air electrodes of metal–air batteries are important applications of inorganic perovskite oxides [15]. The main applications of perovskite oxides for SOFC technology are given in Table 4.

For SOFC cathodes, LaCoO_3 or LaMnO_3 display promise, and LaGaO_3 -based oxides are suitable for the electrolyte, as shown in Table 4. Additionally, some recent studies have suggested that Cr-based perovskites can be used as anodes using perovskite components as the sole building blocks for SOFCs [101]. The growth of SOFC technology using high-temperature proton-conducting electrolytes is marginally behind that of SOFCs using oxide-ion-conducting electrolytes, mainly when compared to the development of polymer electrolyte-type fuel cells [101,102]. Nevertheless, the Toyota group has proven to be very effective when using BaCeO_3 -based electrolyte films on Pd foil for a high-power SOFC [103]. According to their findings, proton-conducting perovskite oxides could become a core driver in real SOFCs in the coming years.

(i). Cathode

The primary concern for the SOFC cathode is that oxygen molecules are electrochemically reduced to oxide. In addition to this, many criteria should be considered, including catalytic operation, thermodynamic stability, and the compatibility of mechanical and chemical properties. To fulfill these cathode specifications, perovskite oxide is the most effective material. Oxygen reduction takes place either on the surface of the electrode or at the interface of gas phase/electrolyte/electrode, which is referred as the “triple phase boundary” (TPB). The material of the electrode catalyzes oxygen molecules into atom dissociation, charging and integrating them into the electrolyte. Electrocatalytic activity is considered to be a significant parameter for cathode material. By calculating the surface reaction rate constant in the oxygen isotope exchange, catalytic activity can be hence calculated [48,104].

(ii). Anode

For SOFC anodes, a cermet ($\text{Ni-Y}_2\text{O}_3$ -stabilized ZrO_2 (BFO, YSZ)) is commonly used, which is a metal-oxide ion-conducting oxide composites. Ni, on the other hand, is well known for being quickly deactivated by accumulation and roughening. Furthermore, Ni re-oxidation is a normal phenomenon, consequent in the cell's irreversible failure. As a result, the use of oxide as an anode has recently been suggested, with La, Nd and other elements doped in SrTiO_3 perovskite oxides, as well as other elements among the proposed oxide anodes doped in SrTiO_3 , etc. [105], or $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{0.5}\text{O}_3$ (LSCrM) [106] which demonstrate promising performance as oxide anodes.

(iii). Electrolyte

For SOFC electrolytes, an oxide ion conductor is commonly used. Solid proton-conducting ceramics such as BaZrO_3 or SrCeO_3 doped with different rare-earth cations to

B-sites were also investigated in the case of SOFCs [103], particularly for low-temperature SOFCs. However, SOFCs using oxide-ion-conducting electrolytes are more promising in terms of their chemical stability and power density. With few exceptions, YSZ is currently the most used as the electrolyte in almost all SOFCs in commercial production processes. In addition, there is still tremendous scope for an alternative electrolyte with higher oxide ion conductivity to replace YSZ in order to increase the power density. For this reason, fluorite-structured CeO_2 and LaGaO_3 with perovskite structures are promising electrolytes. The first perovskite-structured pure oxide ion conductor, LaGaO_3 doped with Sr and Mg (LGSF), is of particular interest [107]. LGSF oxide ion conductivity, as initially observed, is substantially higher than YSZ and is nearly equal to Gd-doped CeO_2 . Partial electron conductivity is exhibited in reducing atmospheres when using CeO_2 , and the pure oxide ion conductivity is exhibited across a wide $p\text{O}_2$ range, i.e., from pure oxygen to pure hydrogen, in the case of LGSF.

9. Plasmonic Perovskite Solar Cells

The implementation of nanoparticles with plasmonic effects is an alternative way for photon and charge carrier control, among the numerous methods for advancing solar cell technologies. Surface plasmons are able to interact through electromagnetic radiation at the interfaces or surfaces of sophisticated metal nanostructures. By engineering the shape, size, and dielectric properties of the metal nanostructures, the properties of surface plasmons can be tuned precisely. PSCs with plasmonic structures permit thinner photovoltaic absorber layers without compromising their thickness while more efficiently harvesting the solar energy [108,109]. Here, the effects of plasmonic nanostructures in electron transport material [110], perovskite absorbers [110,111], hole transport material [110,112] and the enhancement of effective refractive index [113,114] of the medium and the solar cell performance are abridged.

9.1. Plasmonics in Electron Transport Material

In 2015, Yuan et al. [115] introduced a new TiO_x -Au- TiO_x sandwich structure to enhance the PSC performance by incorporating low-temperature-processed amorphous TiO_x , as shown in Figure 11a, whereas real time scanning electron microscopic image of PSC cross-section is given in Figure 11b, with the results tabulated in Table 5. Electrons injected from Au-NP plasma decay filled the trap sites in the TiO_x conduction band. This filling of trapped sites resulted in the surface potential of TiO_x reduction [108,116,117]. This combination has greatly enhanced the PCE up to 16.2%. In particular, improving the efficiency of the device is due to reductions in the TiO_x film's surface potential and improved conductivity.

Figure 11. (a) Schematic of the (ITO/ TiO_x -Au-NPs/ $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ /HTL/Ag) device structure. Gold-NPs are embedded between two TiO_x layers. HTL can be either P3HT or Spiro-OMeTAD. (b) Cross-sectional SEM image of the device. Reproduced with permission from Ref. [118].

Table 5. Electrical output characteristics of the devices with P3HT and Spiro-OMeTAD as HTLs.

HTL	ETL	FF	J_{sc} [mA cm^{-2}]	V_{oc} [V]	R_s [$\Omega \text{ cm}^{-2}$]	PCE [%]
P3HT	Control Device	(0.63 ± 0.02)	(15.4 ± 0.3)	(0.92 ± 0.03)	15.2	(9.03 ± 0.25)
	TiOx/Au-NPs (Embedded)	(0.68 ± 0.01)	(17.1 ± 0.5)	(0.95 ± 0.02)	11.2	(11.3 ± 0.4)
	TiOx/Au-NPs (On top)	(0.53 ± 0.04)	(15.0 ± 0.6)	(0.85 ± 0.02)	16.5	(7.05 ± 0.37)
Spiro-OMeTAD	Control Device	(0.68 ± 0.02)	(18.6 ± 0.3)	(0.97 ± 0.02)	10.8	(12.3 ± 0.6)
	TiOx/Au-NPs (Embedded)	(0.74 ± 0.03)	(19.4 ± 0.2)	(1.02 ± 0.02)	5.25	(14.8 ± 0.5)

9.2. Plasmonics in Absorber Material

In 2013, Wei Zhang et al. [118] reported 11.4% PCE, and the results are summarized in Figure 12d. It was attributed to plasmonic effects of incorporated Au nanoparticles as core-shell Au@SiO₂ nanoparticles (NPs) in meso-superstructured organometal halide perovskite, which led to tangible enhancements in the photocurrent and PCE of solar cells (Figure 12). Enhancement in photocurrent is also attributed to reductions in exciton binding energy due to incorporated/embedded nanoparticles, rather than an enhanced light absorption.

Figure 12. (a) Illustration of device structure with. (b) Typical TEM micrograph of Au@SiO₂ NPs. (c) J–V plots for Al₂O₃-only and Au@SiO₂ devices measured under STC. (d) Load dependence of Au@SiO₂ NPs on the device performance. Reproduced with permission from Ref. [119].

In 2016, Wu R. et al. [120] prepared planar heterojunction (PHJ) PSC with the structure of ITO/PEDOT:PSS/CH₃NH₃PbI₃/PCBM/Al and incorporated silica-coated gold (Au@SiO₂) core-shell nanorods (NRs) to the interface between the CH₃NH₃PbI₃ and PEDOT:PSS (Figure 13). The PCE significantly increased, i.e., to 15.6%, due to Au@SiO₂

NRs incorporation, from a previous value of 10.9%. Efficiencies for different Au@SiO₂ concentrations are given in Table 6. This enhancement was attributed to the localized surface plasmon resonance of Au@SiO₂ NRs, rather than enhancing the incident light trapping and improved transportation and charge carrier collection.

Figure 13. Glass/FTO/Au@TiO₂nanofibers/MAPbI₃/spiro-OMeTAD heterojunction/Au (**left**) with and (**right**) without Au@SiO₂ nanorods.

Table 6. With and without Au@SiO₂ nanorods, PHJ-PSC devices developed JV curves showing the average performance parameters. In parentheses, the best photovoltaic parameters are given.

Concentration of Au@ SiO ₂ Nanorods (pM)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
0	0.99 ± 0.05	18.3 ± 1.2	59.5 ± 4.9	10.9 ± 1.2
0.032	0.95 ± 0.03	18.9 ± 1.7	61.3 ± 2.8	11.2 ± 1.3
0.047	1.04 ± 0.03	20.7 ± 1.0	72.0 ± 3.4	15.6 ± 0.9
0.095	1.01 ± 0.02	20.3 ± 1.0	70.1 ± 1.1	14.5 ± 0.8

In 2016, Mali et al. [121] reported a method for facilitating the generation of plasmon-enhanced charge in PSC by Au-embedded TiO₂ nanofiber prepared by electrospinning, i.e., glass/FTO/Au@TiO₂nanofibers/MAPbI₃/spiro-OMeTAD heterojunction/Au; the performance parameters are summarized in Table 7. Enhancements in the separation of the charge carrier are accredited to the perovskite and Au@TiO₂ nanofibers' defect-free interface and perovskite/TiO₂ grain boundary reductions.

Table 7. TiO₂ and Au@TiO₂ nanofiber-based PSCs hysteresis analysis.

Sample	Scan Direction	FF%	J _{sc} [mA cm ⁻²]	V _{oc} [V]	η [%]
TiO ₂ nanofibers	Forward	59 ± 4	18.57 ± 0.38	0.898 ± 0.02	9.83 ± 0.35
	Reverse	60 ± 4	19.52 ± 0.38	0.953 ± 0.02	11.16 ± 0.35
	Average	59.5	19.045	0.925	10.48
Au@TiO ₂ nanofibers	Forward	64 ± 3	20.16 ± 0.38	0.951 ± 0.02	12.27 ± 0.33
	Reverse	70 ± 2	21.63 ± 0.36	0.986 ± 0.02	14.92 ± 0.33
	Average	67	20.89	0.967	13.53

9.3. Plasmonics in the Hole Transport Material

In 2015, Wang et al. [112] reported that adding Au-NPs into a conjugated poly(3-hexylthiophene-2,5-diyl) (P3HT) resulted in the electrical conductivity and carrier mobility

of the native P3HT film enhancing by approximately fourfold. This was attributed to enhanced polymer chain ordering caused by Au-NPs. An enhancement of 25% in PCE was achieved by incorporating a 20% loading of Au-NPs in P3HT film in perovskite solar cells as HTLs (Figure 14). In Table 8, solar cell efficiencies and other parameters are given, summarizing the effect each Au-NPs (%) loading into the P3HT HTL layer.

Figure 14. (a) J–V characteristics for devices with and without doping of Au-NPs in the HTLs; (b) IPCE curves for devices with and without doping of Au-NPs in the HTLs. Reproduced with permission from Ref. [115].

Table 8. With and without HTL doping with Au-NPs under STC.

Au (%)	R_s [$\Omega \text{ cm}^{-2}$]	V_{oc} [V]	FF	J_{sc} [mA cm^{-2}]	η [%]
0	12.57 ± 2.74	19.06 ± 0.85	56.11 ± 6.04	0.70 ± 0.04	7.81 ± 0.92
10	11.41 ± 2.62	20.02 ± 0.11	61.03 ± 3.04	0.71 ± 0.02	8.76 ± 0.61
20	10.52 ± 2.17	21.53 ± 0.48	60.72 ± 3.86	0.72 ± 0.03	9.82 ± 0.89
30	11.13 ± 2.76	20.87 ± 0.39	58.81 ± 4.22	0.68 ± 0.04	8.13 ± 0.98

9.4. Plasmonics in Semi-Transparent PSCs

Due to potential uses including building-integrated photovoltaics (such as in windows and cladding tiles), automotive applications, and tandem solar cells, semi-transparent solar cells attract considerable interest. The use of thin active layers and island-type structures [15], suppressing scattering by making the interfaces smoother [122], also semi-transparent electrodes [119], is a general approach to semitransparent cells. In solar cells, and more generally, in optoelectronic systems, numerous examples of transparent electrodes have been used, such as thin metal films, conductive polymers [123], carbon nanotubes [124], conductive oxides [125], metal NWs [126], or graphene [102,127]. In tandem solar cells, semi-transparent PSCs can also be applied [128–130]. In 2017, Kim et al. [131] have applied silver nanocubes (Ag-NCs) to utilize electrode-coupled plasmons (ECPs). The ECP wavelength can be modulated relatively easily by adjusting the particle size and the thickness of the semiconductor layer.

In Table 9, we have summarized the plasmonics nanoparticles effects on the perovskite solar cell. The respective, investigated and proposed mechanisms due to the incorporation of different metallic nanoparticles of different sizes, morphologies and concentrations for different configurations and in different layers of the PSCs are also given.

Table 9. Plasmonics nanoparticles applied in perovskite solar cells along with PV performances and mechanisms.

Ref.	Structure	J_{sc} (mA/cm ²)	J_{sc} Enhancement (%)	Efficiency (η %)	Efficiency Increase (%)	Mechanism
[132]	ITO/ PEDOT:PSS/MAPbI ₃ /Ag NPs (79 nm)/PCBM/LiF/Al	19.89 to 24.41	18.5	11.63 to 13.46	13.6%	The improved J_{sc} and overall device performance are attributed to enhanced absorption via LSPR and light optical path length increases
[133]	ITO/Au NPs (120 nm):QD- CsPbBr ₃ / PEDOT:PSS/MAPbI ₃ /C ₆₀ /Ag	20.6 to 22.5	9	8.53 to 10.9	27.8	LSPR excitation and light scattering
[134]	ITO/ PEDOT:PSS/MAPbI ₃ /PCBM/Ag (nanocubes)/BCP/Ag	19.5 to 21.4	9	11.9 to 13.3	10.5	Plasmonic Ag nanocube coupling with Ag back electrode
[135]	ITO/TiO ₂ /ZrN/SiO ₂ NPs (75 nm core/40 nm shell)/MASnI ₃ /Spiro-OMeTAD/Au	27 to 40.3	33	12.9 to 20	35.5	Attributed to enhancement in the plasmonic surface plasmon's directivity by the dielectric shell
	ITO (150 nm)/TiO ₂ (40 nm)/TiN NPs (100 nm)/MASnI ₃ (350 nm)/Spiro-OMeTAD (200 nm)/Au (100 nm)	27 to 36.91	27	12.9 to 18.2	29	Absorption enhancement due to plasmonic NP effects acts as a wave guide to direct sunlight by LSPR, forming surface plasmon polaritons (SPP) at the air/TiN interface
	ITO (150 nm)/TiO ₂ (40 nm)/ZrN NPs (100 nm)/MASnI ₃ (350 nm)/Spiro-OMeTAD (200 nm)/Au (100 nm)	27 to 34.2	21	12.9 to 16.6	22.3	Plasmonic resonance enhancement at NIR wavelengths
[118]	FTO/TiO ₂ (50 nm)/Al ₂ O ₃ (130 nm) with Au (80 nm)@SiO ₂ (8 nm) + MAPbI ₃ /Spiro-OMeTAD/Ag	14.76 to 16.91	13	10.7 to 11.4	6	Attributed to enhanced photocurrent due to enhanced light absorption and plasmonic localized heating

Table 9. Cont.

Ref.	Structure	J_{sc} (mA/cm ²)	J_{sc} Enhancement (%)	Efficiency (η_l %)	Efficiency Increase (%)	Mechanism
[136]	FTO/Ag@TiO ₂ /Al ₂ O ₃ + MAPbI ₃ /Spiro-OMeTAD/Ag	17.3 to 20.2	14.35	11.4 to 13.5	16	Photocurrent improvement due to highly polarizable metallic NPs
[137]	FTO/c-TiO ₂ /m-TiO ₂ /Au-Ag alloy NPs (popcorn-shaped)/MAPbI ₃ /Spiro-OMeTAD/Ag	15.51 to 16.46	6	8.9 to 10.3	15.7%	Plasmonic popcorn NPs lead to faster charge transfer at the TiO ₂ /perovskite interface, resulting in PCE increase
[138]	FTO/TiO ₂ /SnO ₂ /CsFAMAPbI ₃ Br ₃ /Ag NR (buffer layer) Spiro-OMeTAD/Au	21.08 to 22.18	5	18.50 to 20.29	9	Ag NR increased the absorption by LSPR effect
[139]	ITO/TiO ₂ /Au@TiO ₂ (NR)/MAPbI ₃ /Spiro-OMeTAD/Au	20.78 to 22.27	7	15.76 to 16.35	20.10	Facilitated carrier transfer or separation in the presence of plasmonic NPs
[140]	FTO/PEDOT:PSS + Ag NPs/MAPbI ₃ /PCBM/Al	15.06 to 15.47	3	4.17 to 5.58	25.3	Plasmon induced enhanced absorption, superior photo-generated-carrier separation and transport by the Ag-NPs in the active perovskite material
[141]	FTO/c-TiO ₂ /TiO ₂ (nanocolumns, NC)/Cs _{0.05} (FA _{0.83} MA _{0.17}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ /SpiroOMeTAD/Au	19.27 to 20.19	4.6	15.31 to 16.38	6.5	TiO ₂ NC affects the performance of perovskite halide solar cells in terms of the charge transport, light-harvesting, and stability
[142]	FTO/c-TiO ₂ /Au@TiO ₂ NPs embedded in p-TiO ₂ /MAPbI ₃ /Spiro-OMeTAD/Ag	17.40 to 23.12	25	12.59 to 18.24	44	Improvement is associated with exciton generation rate, enhanced exciton dissociation probability, as well as efficient carrier transfer/collection induced by the LSPR effect

Table 9. Cont.

Ref.	Structure	J_{sc} (mA/cm ²)	J_{sc} Enhancement (%)	Efficiency (η_l %)	Efficiency Increase (%)	Mechanism
[143]	ITO/ZnO/MAPbI ₃ /Au (nanostars)/Spiro-OMeTAD/Ag	17.43 to 18.21	4.3	11.98 to 13.97	14	Absorption improved by Au NSs due to SPR and backscattering effects.
[144]	FTO/ZnO/ZnO NR/MAPbI ₃ /spiro-OMeTAD/Au	18.07 to 20.56	12.1	14.51 to 16.77	~14	LSPR
[133]	120AuNPs: Quantum Dots (QD)-CsPbBr ₃ / PEDOT:PSS/MAPbI ₃	20.6 to 22.5	8.4	8.53 to 10.9	~27.8	LSPR excitation by resonance interaction
[145]	ITO/ PEDOT:PSS/ CH ₃ NH ₃ PbI ₃ / PC ₆₁ BM/Al	16.70 to 18.15	8	10.54 to 11.74	~10.22	Sub-wavelength antenna due to LSPR excitation

10. Summary and Outlook

Due to their extensive intriguing physical and chemical properties, perovskite oxides have evolved as an attractive class of materials, garnering intense research interest in condensed matter physics and a range of functional device applications. Among several practical materials, perovskite oxides have demonstrated a large variety of applications closely related to people's lives. The market for applications has been dominated by the wide use of high-performance perovskites in memory, sensors, microelectronics, piezoelectric actuators, energy harvesting and storage systems, mechanical processing, ultrasonic energy converters, and optical and other related optoelectronic devices.

The crystal structures of perovskites and associated oxides have been described throughout this study. Perovskite oxide is composed of a number of materials and components. Furthermore, in the crystals structure there are several polymorphs. Therefore, there are several functions and rich application areas dependent on the wide range of crystal structures. A brief overview of the use of perovskite oxides for photocatalytic properties and solid oxide fuel cells has been provided. Perovskite oxides are commonly used for SOFCs and oxygen permeation membranes because a high electrical conductivity and a surface activity for oxygen dissociation are obtained instantaneously. On the other hand, Ta- or Ti-based perovskites are highly active when applied to photocatalysts. An overview of the recent developments in plasmonic nanostructures in PSCs, including semi-transparent devices, is also presented in this study. Machine learning models trained on extensive experimental and computed databases to assess the stability of various oxide perovskites polymorphs have revealed that the chemical composition is far from being fully explored. A recent study predicted that about 500 single and double perovskites remained unreported. Considering the diverse domains of applications of oxide perovskites covered in this review, potential novel candidates predicted computationally then synthesized in the lab might help broaden the spectrum of applications to target niche technological areas.

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Abbreviations

AFM	Atomic force microscopy
BCO	BiCrO_3
BFO	BiFeO_3
BMO	BiMnO_3
BSCF	$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$
BTO	BaTiO_3
CIGS	CuInGaS
DMI	Dzyaloshinskii–Moriya interaction
ECPs	Electrode-coupled plasmons
ETL	Electron transport Layer
FM	Ferromagnetic
HTL	Hole transport layer
I_{sc}	Short-circuit current
LAO	LaAlO_3
LGSM	LaGaO_3 doped with Sr and Mg
MBE	Molecular beam epitaxy
MOCVD	Metal organic chemical vapor deposition
NRs	Nanorods

PCE	Power conversion efficiency
PFM	Piezoelectric force microscopy
PHJ	Planar heterojunction
PLD	Pulsed laser deposition
PSCs	Perovskite solar cells
PV	Photovoltaics
RE	Rare-earth
RHEED	Reflection high-energy electron diffraction
SG Transition	Spin glass transition
SOFCs	Solid oxide fuel cells
SOTA	State-of-the-art
SSO	Spiral spin order
STC	Standard test conditions
T _c	Curie temperature
T _{FE}	Ferroelectric temperature
T _{FM}	Ferromagnetic temperature
TMO	Transition metal oxide
TWC	Three-way catalyst
V _{oc}	Open-circuit voltage
YMO	YMnO ₃
YSZ	Y _{0.16} Zr _{0.84} O ₂

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