

Origin And History of Perovskite compounds

- Perovskite is calcium titanium oxide or calcium titanate, with the chemical formula CaTiO_3 .
- Very stable structure, large number of compounds, variety of properties, many practical applications.
- Key role of the BO_6 octahedra in ferromagnetism and ferroelectricity.
- Extensive formation of solid solutions
- material optimization by composition control and phase transition engineering.



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Perovskite

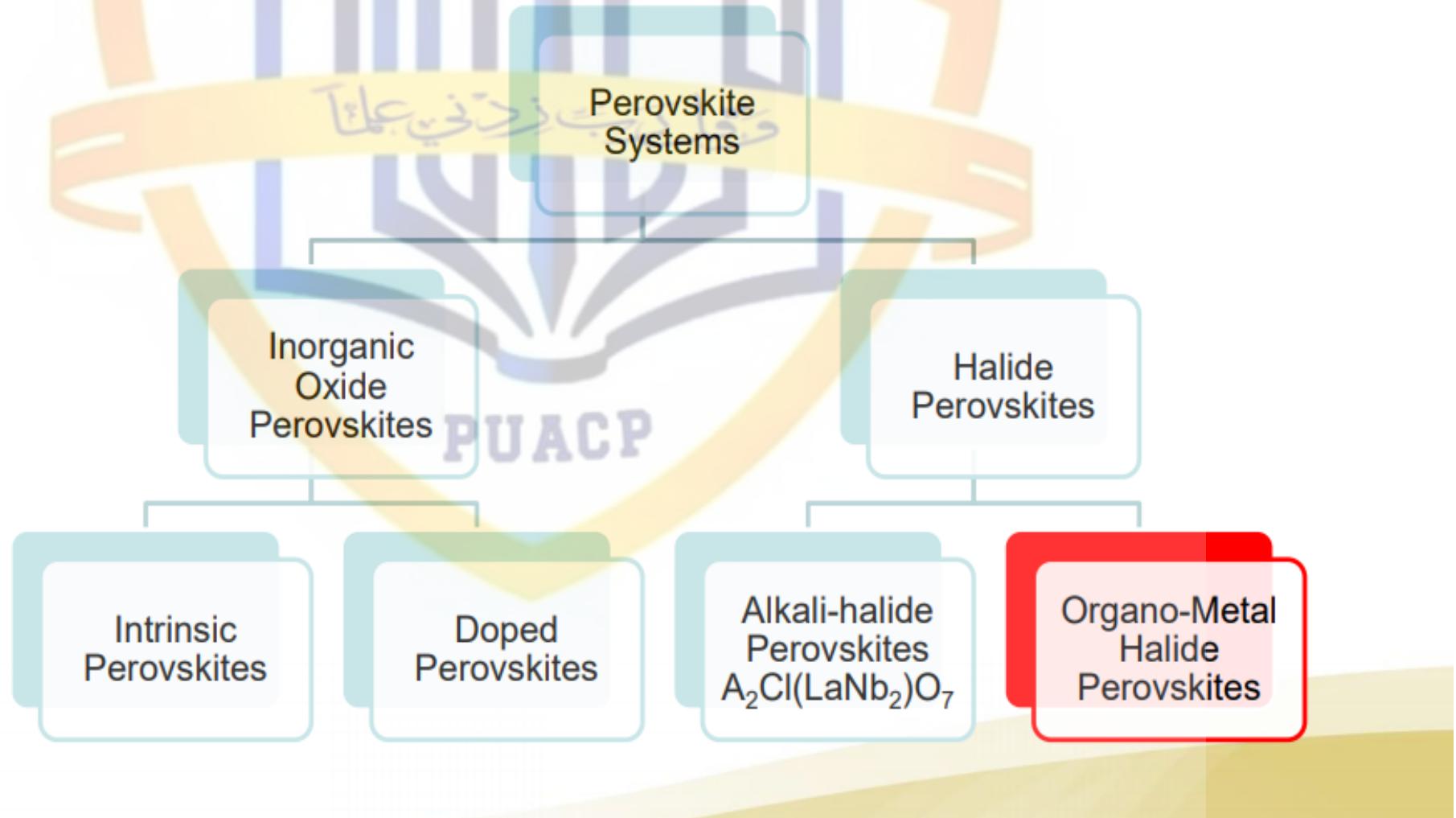


Orthorhombic perovskite ABO_3



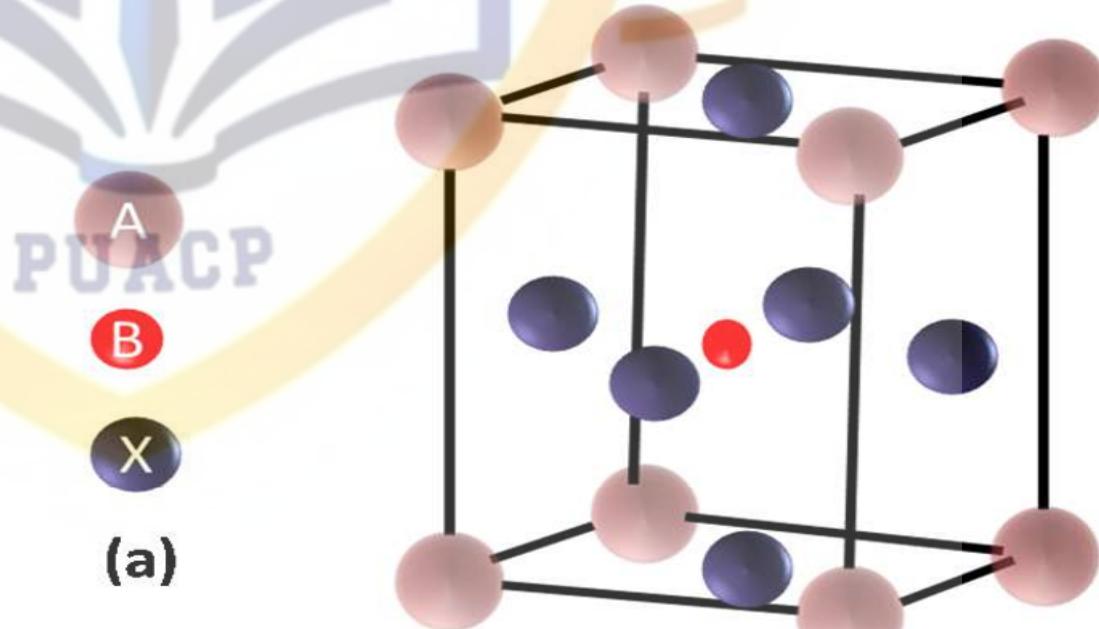
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Classification of Perovskite System



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- Organometal halides ($\text{CH}_3\text{NH}_3\text{PbX}_3 = \text{ABX}_3$, where A = CH_3NH_3^+ , B = divalent metal, i.e., Pb^{+2} and X⁻ = halide ion) based perovskite semiconductors have shown excellent performance in solar cells^{3,4,5,6} application and optical gain.



Typical crystal structure of organometallic halide (ABX_3) where A is for Alkylamine (R-NH_3), B is for divalent metal (Pb^{+2}) and X is for halide ion (X^-).



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Importance of Perovskite Material

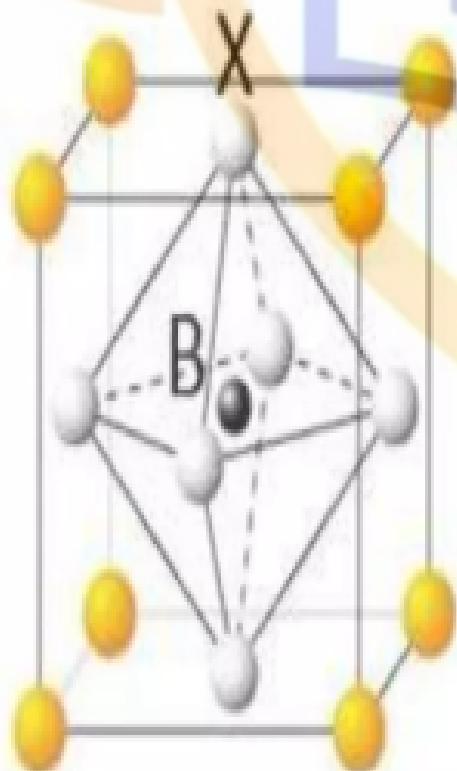
- Advantage
 - direct optical band gap of around 1.5ev.
 - long diffusion length
 - long minority carrier lifetimes
 - Broad absorption range from visible to near-infrared spectrum(800nm)
- Disadvantage
 - Degradation of methyl ammonium lead iodide perovskite



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INTRODUCTION

Introduction



Perovskite is Calcium Titanium Oxide or Calcium Titanate, with the chemical formula CaTiO_3 . The mineral was discovered by Gustav Rose in 1839 and is named after Russian mineralogist Count Lev Alelseevich Perovski (1792-1856).

All materials with the same crystal structure as CaTiO_3 , namely ABX_3 , are termed perovskites.

The perovskite lattice arrangement is demonstrated below. As with many structures in crystallography, it can be represented in multiple ways. The simplest way to think about a perovskite is as a large atomic or molecular cation (positively-charged) of type B in the centre of a cube. The corners of the cube are then occupied by atoms A (also positively-charged cations) and the faces of the cube are occupied by a smaller atom X with negative charge (anion).

Key role of the BX_6 octahedral in ferromagnetism and ferroelectricity.

A(valences +1, +2)

B(valences +3, +4)

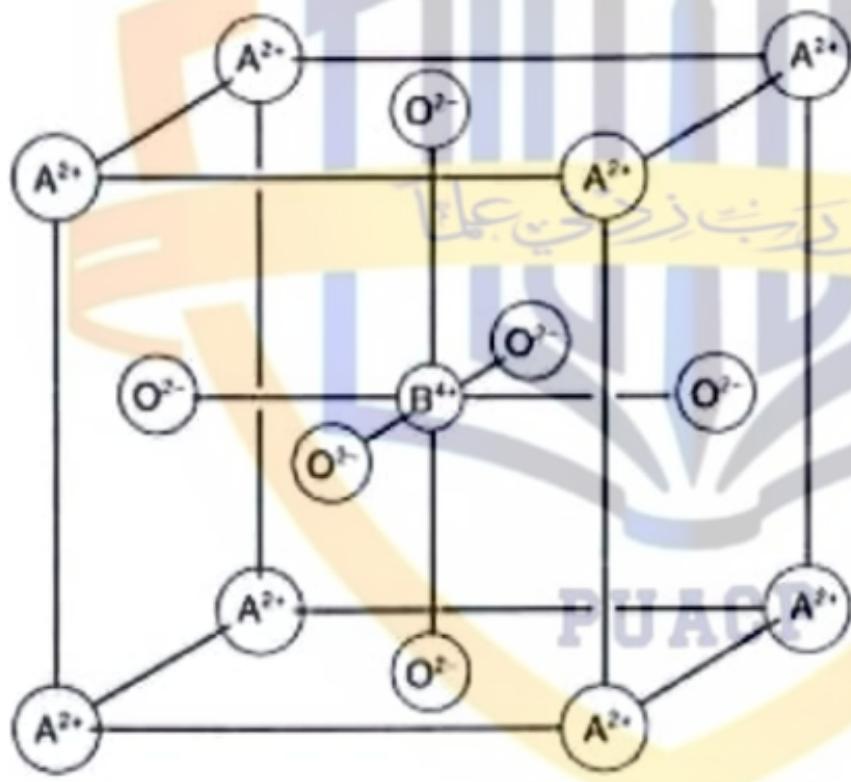


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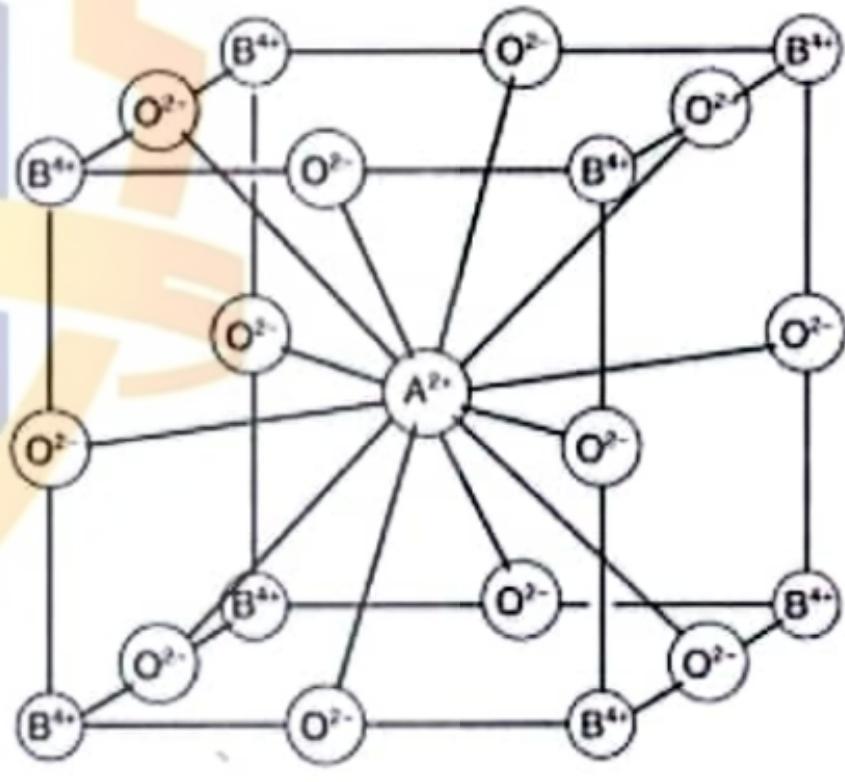
Another important class of mixed-metal oxides are the **perovskites**, ABO_3 , of which the prototype is CaTiO_3 (perovskite). It has an unusual ccp lattice of oxide and calcium ions (Fig. 13.6), in the octahedral holes of which the much smaller Ti^{4+} ions can “rattle around”.

There are many other perovskites, which can be generated from the structure of CaTiO_3 through the application of either the first or the second principle of **isomorphous substitution**. This latter principle allows more versatility: although substituting ions must still be about the same size as the ions replaced in order not to change the lattice type, within certain strict limits the *charge* of the entering ion need not be identical to the charge of the departing ion. The basic principle is that the *total* charge of the replacing ions must equal the total charge of the replaced ions. This means that isomorphous substitution can occur even if the new ion C have a charge one greater than the old ion A, *if there is simultaneous substitution by a new ion D with a charge one less than the old ion B*. This conserves the electroneutrality of the salt, since the sum of charges of the new ions C and D equals the sum of charges of the old ions A and B.





(a)



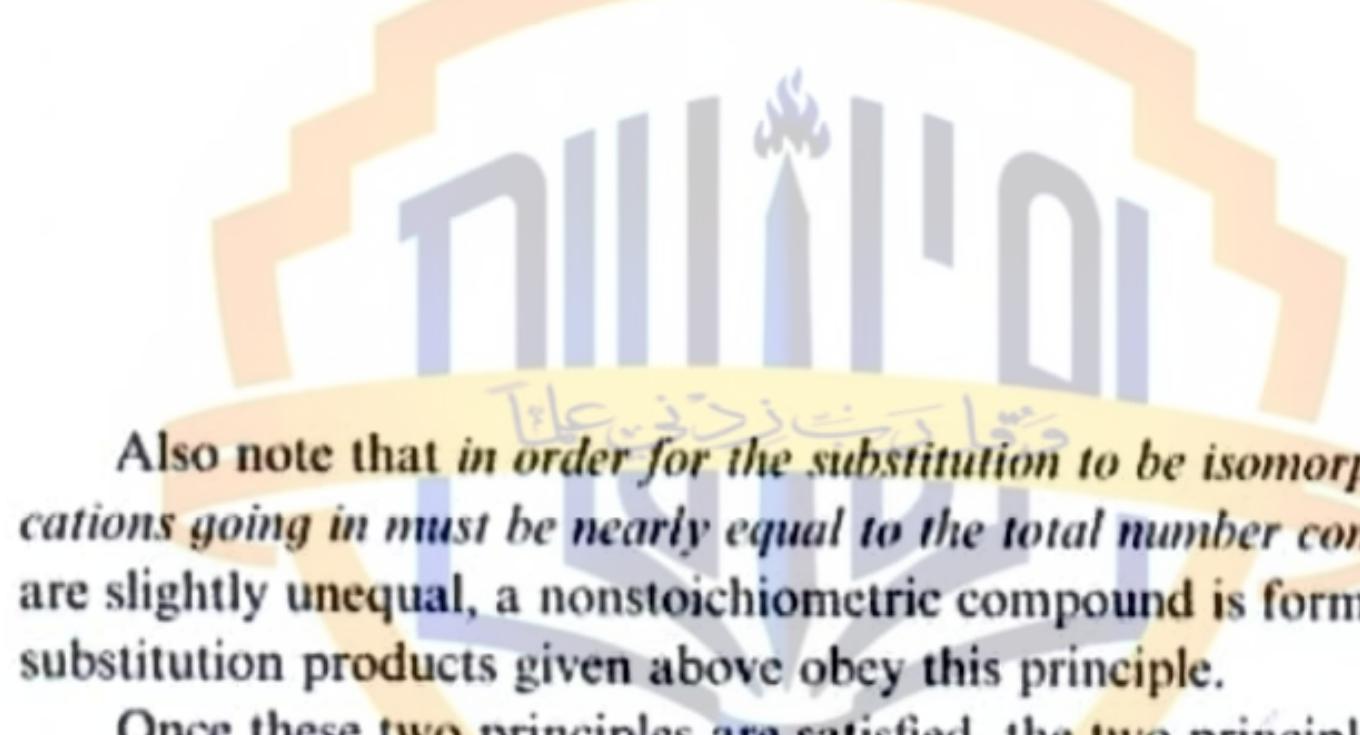
(b)

Figure 13.6

The structure of perovskites, ABO_3 (e.g., $\text{A}=\text{Ca}^{2+}$, $\text{B}=\text{Ti}^{4+}$ in CaTiO_3), shown (a) with B^{4+} at the center of the unit cell and emphasizing the octahedral coordination of B^{4+} , (b) with A^{2+} at the center of the unit cell and emphasizing the dodecahedral (12) coordination of A^{2+} .



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Also note that *in order for the substitution to be isomorphous, the total number of cations going in must be nearly equal to the total number coming out.* (If the two numbers are slightly unequal, a nonstoichiometric compound is formed.) All four possible substitution products given above obey this principle.

Once these two principles are satisfied, the two principles of isomorphous substitution are satisfied if the cations going into the replacement structures are within 10–20% of the radii of the cations coming out. In (a), Y^{3+} has a radius of 104 pm, which is too much bigger than Al^{3+} (67 pm) for the substitution to be isomorphous. However, (b) and (c) are satisfactory, since in (b) Rb^+ (166 pm) is close in size to K^+ (152 pm), and in (c) Ba^{2+} (149 pm) is close to K^+ (152 pm), and Be^{2+} is close to Al^{3+} .



The perovskite structure type requires that the sum of the charges of the A and B metal ions be +6 and that they be quite different in size from each other. Thus, other perovskites such as $\text{Li}^+ \text{Nb}^{5+} (\text{O}^{2-})_3$ are also known, as are fluoride perovskites such as $\text{Na}^+ \text{Fe}^{2+} (\text{F}^-)_3$. If the temperature is not too high, the Ti^{4+} ions of perovskite itself tend to be off the center of the lattice unit cell, giving rise to an electric charge separation or dipole. Such materials are known as ferroelectrics. Application of mechanical pressure to one side of a perovskite crystal causes the Ti^{4+} ions to migrate, generating an electrical current; application of an electric current causes mechanical motion of the ions. The pressure effect, known as the piezoelectric effect,³² makes perovskites and the form of SiO_2 known as quartz useful in converting mechanical energy to electric energy, as in microphones, sonar, and vibration sensors, or vice versa. The conversion of electrical energy to mechanical energy is useful in sonic and ultrasonic transducers and in headphones and loudspeakers.



a. Dielectric property

There are some properties inherent to dielectric materials like ferroelectricity, piezoelectricity, electrostriction, and pyroelectricity. **One of the important characteristic of perovskites is ferroelectric behaviour, which is obvious in BaTiO₃, PdZrO₃ and their doped compounds.**

The ferroelectric behaviour of BaTiO₃ was strongly related to its crystal structure. BaTiO₃ was subjected to three phase transitions; as the temperature increases, it was converted from monoclinic to tetragonal then to cubic. At temperature higher than 300K, BaTiO₃ does not show any ferroelectric behaviour as it crystallizes into cubic structure. Rather, it showed high dielectric constant.

Worthy of note:

Yttrium barium copper oxide can be insulating or conducting depending on oxygen content.

The oxygen nonstoichiometric is one of the most significant reasons for the high value of T_c. It crystallizes into orthorhombic structure, which is superconductive, it showed a tetragonal structure that does not show any superconductivity.

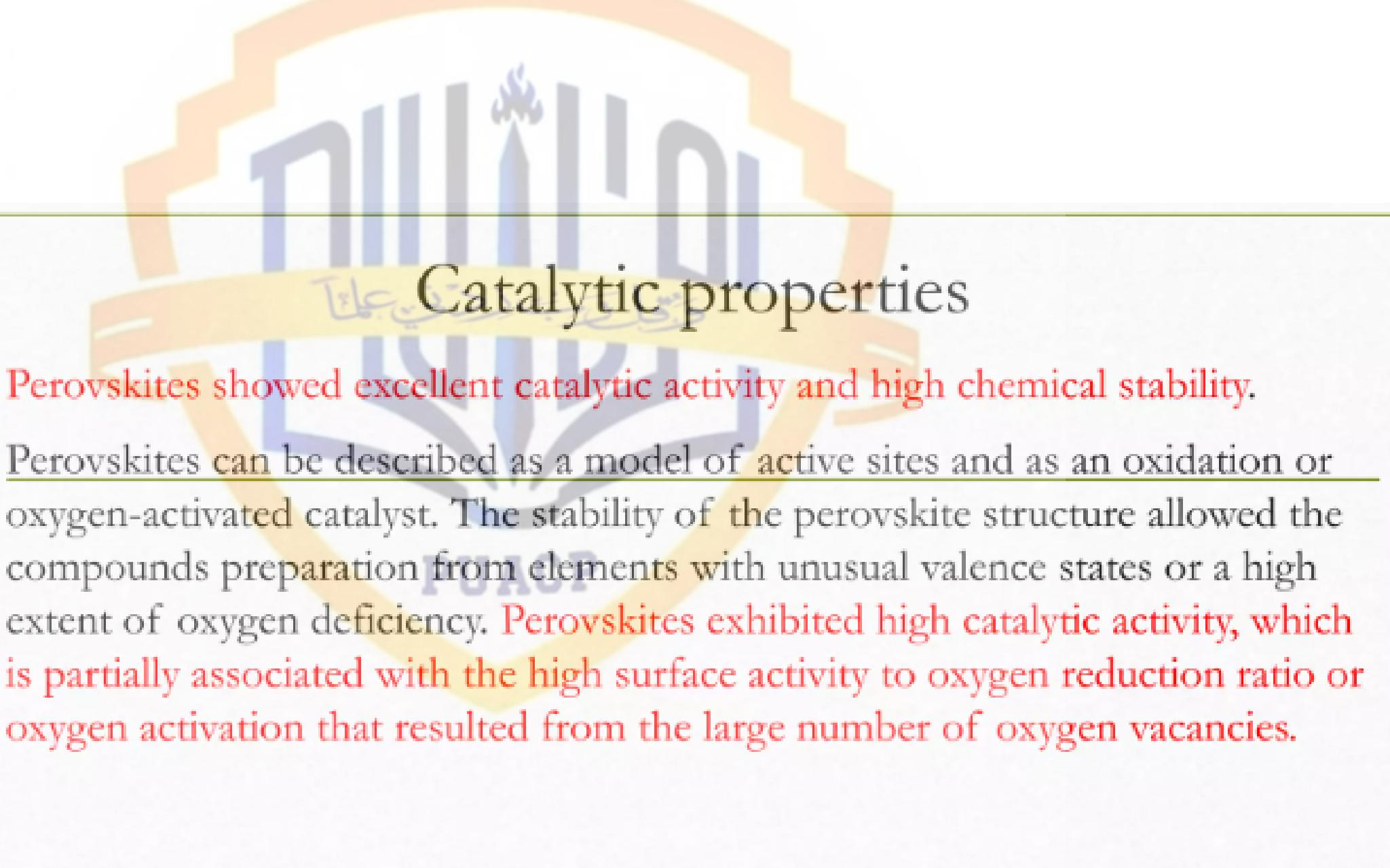
Electrical conductivity

Cu-based perovskites act as high-temperature superconductors. The presence of Cu in A-site is essential for the superconductivity and various superconducting oxides can be manufactured with different B-site ions.

The electronic conductivity of the perovskites can be enhanced by doping the A-site with another cation, which resulted in increasing the quantity of the mobile charge carriers created by the separations of charge.



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Perovskites showed excellent catalytic activity and high chemical stability.

Perovskites can be described as a model of active sites and as an oxidation or oxygen-activated catalyst. The stability of the perovskite structure allowed the compounds preparation from elements with unusual valence states or a high extent of oxygen deficiency. Perovskites exhibited high catalytic activity, which is partially associated with the high surface activity to oxygen reduction ratio or oxygen activation that resulted from the large number of oxygen vacancies.



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Optical properties

Although there are a lot of challenges in determining with certainty the optical properties of perovskites (still under research). Progress in this area has been hindered by the difficulty of producing continuous films of sufficient smoothness and neglect of some morphological contributions(band structure) which affect optical transition and further complicate accurate determination of the absorption coefficient and other optical parameters of perovskite films.

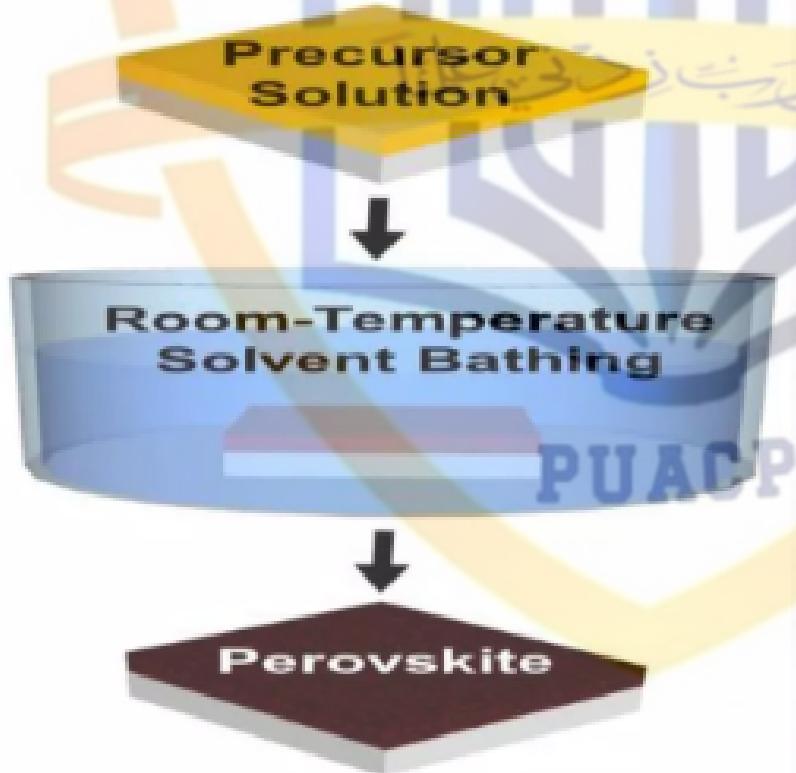
However, hybrid perovskites (especially lead-halide perovskite) have recently received a lot of attention due to **high photoluminescence and quantum yields**.

It has high optical absorption coefficient, excellent charge carrier transport (crystallinity).



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Processing



Perovskite solar cells hold an advantage over traditional silicon solar cells in the simplicity of their processing. Traditional silicon cells require expensive, multistep processes, conducted at high temperatures ($>1000\text{ }^{\circ}\text{C}$) in a high vacuum in special clean room facilities. Meanwhile, the organic-inorganic perovskite material can be manufactured with simpler wet chemistry techniques in a traditional lab environment. Most notably, methylammonium and formamidinium lead trihalides have been created using a variety of solvent techniques and vapour deposition techniques, both of which have the potential to be scaled up with relative feasibility.



1. Photovoltaics:

The performance of metal halide perovskite solar cells has made rapid increases in energy conversion efficiency, improving from under 4% efficiency in 2010 to a record efficiency of 22% in 2016. Because of the high absorption coefficient, a thickness of only about 500nm is needed to absorb solar energy.



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Applications

(1-3: optical properties, 4: electrical properties)

2. Light Emitting Diodes

~~Due to their high photoluminescence quantum efficiencies, perovskites may be good candidates for use in Light-Emitting Diodes (LEDs).~~ However, the propensity for radiative recombination has mostly been observed at liquid nitrogen temperatures

3. Lasers

In 2008 researchers demonstrated that perovskite can generate laser light. LaAlO_3 (Lantanum Aluminate) doped with neodymium gave laser emission at 1080nm. In 2014 it was shown that mixed methylammonium lead halide ($\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$) cells fashioned into optically pumped Vertical-Cavity Surface-Emitting Lasers (VCSELS) convert visible pump light to near-IR laser light with a 70% efficiency.

4. Electromechanical devices, transducers, capacitors, actuators etc. due to dielectric property(energy storage).



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Current challenges

1. Toxicity: this is due to the lead deposits.
2. Short duration: Study shows that it can maintain only about 80% of its initial efficiency after 500 hours. Researchers from ICL have showed that superoxides are responsible for this. When light hits perovskites, electrons are released and react with oxygen to form superoxides. So glass is used to prevent material from oxidation although more recently, coating with iodide to fill up vacancies(defect) reduces the chance for oxidation.
3. Scaling problem: Production is still on a small scale.



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