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Research Seminar

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Magnetic, Charge Transport, Electrocatalytic, and Pseudocapacitive Properties of Perovskite Oxides

Abstract

Herein, we explore magnetic, electrical, gas sensor, electrocatalytic OER and HER, and pseudocapacitive properties of four different groups of perovskite oxides as shown in Figure 1.[1-4] Perovskite oxides are functional materials with the general formula ABO_3 (A = alkali, alkaline earth, or lanthanide cations; B = transition metal or main group cations). A subclass of the perovskite family, double perovskite, has general formula $AA'BB'O_6$ (Figure 1) and may feature an ordering pattern with corner-sharing of alternating BO_6 and $B'O_6$ octahedral units.[5] Similarly, another derivative class of the perovskite is the oxygen-deficient perovskite oxides (ODPs). In these $ABO_{3-\delta}$ type systems, oxygen-deficiencies (δ) give rise to several coordination geometries for the B-site cations, ranging from octahedral to tetrahedral and square pyramidal (Figure 1).[6] The oxygen-vacancies are distributed randomly [7] or ordered to give a well-known structure called brownmillerite structure.[6] This structure can be generalized by the formula $ABO_{2.5}$ ($\delta = 0.5$) or $A_2B_2O_5$. The structure consists of sequential stacks of tetrahedra (T) and octahedra (O), forming TOTOT…, with an A-site cation residing between the layers. Additionally, a less common ordering scheme in ODP with the ideal formula $ABO_{2.67}$ or $A_3B_3O_8$ does exist. Such type of structural variant is sometimes called the Grenier phase.[8] This structure consists of bilayer stacks of octahedra alternating with a single layer of tetrahedra, i.e., TOOTOOT….

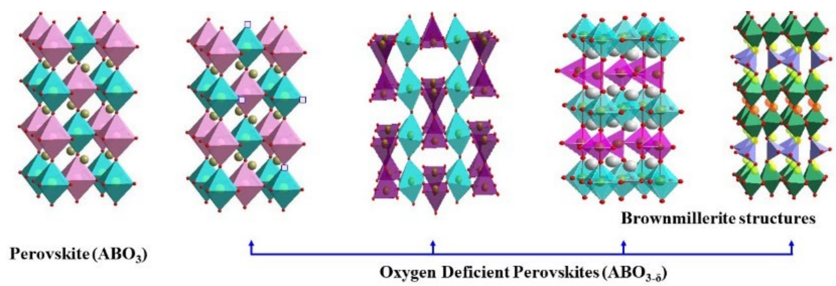

Figure 1. Structural variants in perovskite oxides.

Many properties can be found in this class of compounds, particularly the ones containing earth-abundant metals. Here, the double perovskite oxides $BaSrMnMoO_6$, $BaSrCoMoO_6$, and $BaSrNiMoO_6$ having cubic structures, show contrasting magnetic properties as compared to $BaSrFeMoO_6$. The latter compound has a ferrimagnetic ordering of the magnetic moments of Fe^{3+} ions, while the other three compounds bear antiferromagnetic ordering. Similarly, ODPs are another subclass of the perovskite family for which high-temperature gas sensing properties have not been well documented before. In comparison to compounds $Sr_2Fe_2O_5$, Sr_2FeMnO_5, and Ca_2FeMnO_5 with doping on both A- and B-sites to obtain both ordered and disordered defects in the structure, we explore the structural stability of $Ca_2Fe_2O_5$ brownmillerite being capable of sensing three different gases namely O_2, CO, and CO_2 at 700 °C. We argue based on the underlying mechanisms that the ordered oxygen vacancies having a stable brownmillerite structure play a crucial role in sensing various partial pressures of the analyte gases. We also investigated electrocatalytic properties of ODPs, which resulted in the discovery of a remarkable electrocatalyst $CaSrFeMnO_{6-\delta}$ for catalyzing OER and HER of water splitting. Such a catalyst, which is able to catalyze HER in both acidic and basic media, is rare. This catalyst even surpasses the activity of the state-of-the-art catalysts toward OER. Such property is realized by the combined effect of defect concentration, charge transport properties, and structural stability in several electrolytes. Therefore, perovskite oxides with or without the variation in the arrangement of oxygen-vacancies and the subsequent structural characteristics result in a wide range of properties.

References

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