

Creating novel materials and combinations of materials is thus a critical component that enables the exploration of such fascinating phenomena. The power of advanced materials synthesis has been demonstrated in a large number of instances; for example, semiconductor epitaxy has led not only to a large number of technologies, also to several Nobel prizes. Researchers in oxide science have taken a page out of the semiconductor lexicon and consequently, materials synthesis plays a critical role in enabling the study of such novel materials. In this paper, the recent advances in the growth and characterization of multiferroic and magnetoelectric oxide materials (in particular the model multiferroic BiFeO_3) and the interplay between synthesis, theory, and experimental probes will be reviewed. We will summarize with a look to the future of complex oxide materials with special attention given to possible areas of impact for future technologies.

2. The crystal chemistry of complex oxides

The general field of metal oxide materials has been the focus of much study because of the broad range of structures, properties, and exciting phenomena present in these materials [1,2]. The perovskite structure, which has the chemical formula ABO_3 (i.e. CaTiO_3 , SrRuO_3 , BiFeO_3), is made up of corner-sharing octahedra with the A-cation coordinated with twelve oxygen ions and the B-cation with six. The structure can easily accommodate a wide range of valence states on both the A- and B-sites (i.e. $\text{A}^{+1}\text{B}^{+5}\text{O}_3$, $\text{A}^{+2}\text{B}^{+4}\text{O}_3$, $\text{A}^{+3}\text{B}^{+3}\text{O}_3$) and can exhibit complex defect chemistry (including accommodation of a few percentage of cation non-stoichiometry, large concentrations of oxygen vacancies, and exotic charge accommodation modes ranging from disproportionation to cation ordering and beyond) that maintains charge balance in the structure [3]. One of the most interesting aspects of complex oxides is our ability to engineer or tune their physical properties simply by replacing, substituting, or varying the ratio of the cationic species that are located at the A- and B-sites of the structure. Selection of the appropriate alloying species (chosen to have different formal valence, ionic radius, etc.) can dramatically impact the structural, electronic, magnetic, polar, etc. properties of these materials. In the end, the electronic structure and coordination chemistry of the cationic species control the fundamental physical phenomena manifested in these materials – producing phases that are insulators, metals, superconductors, ion conductors, possess polar distortions and electromechanical responses, magnetic order, and beyond.

The in-depth work in this field has produced a number of design algorithms that allow one to fundamentally manipulate the properties in these perovskite phases and provide guidelines by which one can engineer their properties. As an example, let us consider the case of the prototypical perovskite SrTiO_3 , which is a good insulator as a consequence of the closed shell electronic structure of both Sr (2+) and Ti (4+ and d^0). From a band perspective, the

valence band (predominantly oxygen 2p in character) is filled while the conduction band (predominantly Ti 3d in character) is empty. Simply changing the A-site cation from Sr to La, however, makes a dramatic difference in the electronic structure as well as in the transport properties. In LaTiO_3 , the Ti is in the 3+ oxidation state and thus in a formal sense has a d^1 electronic structure. As such, it is expected to be a good electrical conductor; however, the reality is something dramatically different. LaTiO_3 is actually a very good insulator; a so-called Mott insulator [4]. This insulating behavior arises due to the interplay between the kinetic energy of the electron and Coulombic repulsion effects at the atomic scale. In mixed A-site compounds (i.e. $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$), these two terms trade off one another and the manifested transport properties are the result of this competition. Such materials exhibit strong (sometimes colossal) changes in their transport properties under external thermodynamic stimuli (i.e. temperature, magnetic field, electric field, chemical potential, etc.). Taking this one step further, if one were to take the LaTiO_3 structure and change the cation at the B-site (the transition metal site), for instance by replacing the Ti with Mn, then one will obtain the antiferromagnetic insulator (insulating for the same reason as for LaTiO_3) LaMnO_3 . There are a number of exquisite treatises on the nature of electronic conduction in oxides (see, for example, Refs. [4,5]) and so we will not elaborate further on this subject here, except to note that the entire evolution of the physics and chemistry of these materials and their implementation into next-generation technologies are dependent on the complex interplay between the cationic stereochemistry, electronic structure, and the interactions among them.

Among the most important aspects in understanding any class of materials is understanding the role of and how to control point defects in materials. In traditional semiconductor systems this control meant mitigation of defects so that one can achieve the true intrinsic electronic properties desired. The study of defects in oxides has a long and rich history. From fast ionic conduction in non-stoichiometric oxides [6] to superconductivity in hole-doped cuprates [7–9] to colossal magnetoresistance in alloyed manganites [10], defects can be essential in defining the properties and performance of oxide materials. Additionally, the multi-component oxide systems, such as the perovskites, are susceptible to complex defect structure development, including compensating densities of cationic vacancies, oxygen vacancies, and the formation of defect complexes (i.e. clusters of defects that exhibit different energetics and behavior from single point defects). For an in-depth review of defects in oxide materials the reader is directed to Refs. [3,11].

3. Multiferroism and magnetoelectricity

A hallmark of perovskites is the large variety of functional responses such as ferroelectricity, piezoelectricity, pyroelectricity, ferromagnetism, antiferromagnetism, etc.,