

# Cation Ordering in Complex Oxides.

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## Abstract.

Several recent papers have addressed the fundamental aspects of the stability and kinetics of ordering in complex oxides, and investigated systems where the properties are mediated by the degree of order. Cation ordering reactions have been shown to induce large alterations in the dielectric, ferroelectric, magnetic, and electronic response of many complex oxides. The majority of the cited publications focus on ion ordering in perovskite related structures; however, additional examples include the ordering of structural slabs and formation of modulated intergrowth structures.

## Introduction.

Cation order/disorder transitions play a critical role in mediating the stability, crystal chemistry, and properties of many solid state systems. For complex oxide systems variations in

the degree of order can induce significant alterations in, for example, magnetic behavior, electronic and ionic conductivity, magneto-resistance, and dielectric/ferroelectric properties. This review focuses on publications from the last year, which have assessed either the fundamental aspects of order/disorder reactions in oxides or their effect upon a property response. The primary area of concentration is the substitutional ordering of cations, where two or more metal species exhibit differing degrees of long or short-range order on a set of structural sites. However, examples involving the ordering ions and vacancies, and different anions are also discussed. Excluded from this analysis is the related topic of charge ordering in oxides, which involves correlations between the different oxidation states of a single metal species. Reviews of this type of order, which is very relevant to the behavior of Colossal Magneto-Resistive (CMR) oxides, can be found elsewhere. [1]

The review begins with a brief summary of papers that have investigated the fundamental aspects of the thermodynamics and kinetics of order/disorder reactions. The majority of the systems selected for the remainder of the review illustrate how order-disorder phenomena in perovskite-related structures can be important for control of properties. The review concludes with formation of intergrowth structures and a series of examples where the order involves modulations of specific structural slabs as opposed to individual ions.

### **Fundamental Studies.**

Most recent investigations of the thermodynamics and kinetics of order/disorder reactions in inorganic systems have appeared in the mineralogical literature. [2,3,4] In this field characterizing and predicting the stability, rate, and mechanisms of ordering reactions is critical to geo-thermometry, geo-barometry, and geo-speedometry and can permit detailed analysis of the cooling history of mineral systems. The volume changes accompanying the ordering are also important in determining phase stabilities under high pressure conditions, and in certain cases (e.g.  $\text{MgTi}_2\text{O}_5$ ) induce large changes in compressibilities. [5,6] A variety of diffraction and spectroscopic methods have been applied to characterize the degree of order in olivines, spinels, feldspars, and other mineral systems, and extensive efforts have been made to characterize and model the response of the order to changes in T and P. The most sophisticated and quantitative models for the thermodynamic aspects of these reactions have applied a Landau approach to convergent and non-convergent ordering. [2,6-8] In the former two (or more) crystallographic

sites become related when their average occupancy becomes equivalent. In this case the ordering produces a reduction in symmetry. In non-convergent ordering the sites never become related by symmetry, even if their occupancies are identical, because of a difference in local coordination or bonding (e.g. spinels). While expressions for the free energy of ordering in convergent systems have been developed for some time, it is only recently that Landau-based theory was adapted to non-convergent order. [6-8] The kinetics and mechanisms of substitutional order-disorder reactions have also been examined and modeled using Ginzburg-Landau rate laws. [2,] Most recently this approach was utilized in studies of the kinetics of Mg/Fe order in  $\text{MgFe}_2\text{O}_4$  spinels [4], and of Al/Ge order in  $\text{BaAl}_2\text{Ge}_2\text{O}_8$  feldspars.[10]

### **B-site Ordering in Dielectric/Ferroelectric Perovskites.**

In addition to supporting many unique electronic responses (colossal magneto-resistance, superconductivity, ferroelectricity, etc.), the  $\text{ABO}_3$  perovskite structure is able to accommodate a broad spectrum of chemical substitutions making it an ideal platform for probing correlations between chemistry, order, and properties. The permutations for inducing order in perovskites include mixed-metal cation order on the A- and B-site positions, and vacancy/mixed-anion order on the oxygen sub-lattice. Several recent publications have focused on cation order in perovskites with a 1:2 mixture of divalent and pentavalent cations on the B-site sub-lattice ( $\text{A}^{2+}(\text{M}^{2+}_{1/3}\text{M}^{5+}_{2/3})\text{O}_3$ , A = Ba, Sr, Pb ;  $\text{M}^{2+}$  = Mg, Zn, Ni, etc.;  $\text{M}^{5+}$  = Nb, Ta). The importance of the “1:2” B-site systems is derived from their relaxor ferroelectric and piezoelectric properties (e.g.  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  – PMN), and from their application as temperature compensated, low-loss dielectrics in wireless microwave communications devices (e.g.  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$  – BZT).

For the Ba-based members of the 1:2 perovskite family small alterations in the degree and symmetry of the order on the B-site sub-lattice can induce order of magnitude changes in their dielectric loss properties. In references [11-13] a direct connection was established between alterations in the degree and length scale of the cation order, and the changes in the dielectric losses of BZT,  $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$  (BMT), and  $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (BMN) based ceramics. The high losses of partially ordered BZT were found to arise from the formation of elastically strained ordering-induced domain boundaries; in the absence of any added substituents the losses could only be improved by reducing the volume of the boundaries through extended high temperature heat treatments. However, when small concentrations ( 3 mole %) of  $\text{BaZrO}_3$  were

substituted into BZT two orders of magnitude improvements in the loss were achieved without the need for extended thermal treatment.[11] The loss improvements were attributed to the stabilization of the domain boundaries by the partial segregation of the Zr cations. Additional anomalies in the losses at 4 and 25 mole % substitution of BaZrO<sub>3</sub> were associated with a cation ordering transition from the 1:2 order in the BZT end-member to a new phase with a “1:1” ordered, doubled perovskite, “random site” structure. The alterations in the cation order in this system also provide a good example of the success of first principles calculations in modeling the stabilities of different cation ordering schemes. In particular the transitions observed by experiment in the BZT-BZ system were reproduced by Bellaiche et al. using calculations based on an electrostatic model.[14]

The B-site cation order in the corresponding Pb-based 1:2 relaxor ferroelectric perovskites (e.g. PMN) has been the subject of considerable debate. In contrast to their Ba and Sr counterparts, none of the Pb systems exhibit “stoichiometric” 1:2 cation order. Instead they adopt a 1:1 doubled perovskite structure that contains an ordered arrangement of two different cation sites. Although the order has been extensively examined, controversies exist regarding the composition of the cation sites and the relationship of the ordering to the relaxor properties of PMN. In the as-sintered forms of the PMN-type systems the 1:1 order is confined to small nano-sized domains that are dispersed in a disordered perovskite matrix. Because of the apparent absence of any growth of the ordered nano-domains with extended thermal annealing, for many years the ordering was interpreted using the “space charge” model. In this charge-imbalanced model the nano-domains were claimed to contain a 1:1 ratio of Mg and Nb, with electro-neutrality being maintained by an Nb-rich matrix. However, a series of new studies have demonstrated that large domain, fully 1:1 ordered PMT (Pb(Mg<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub>) and PMN relaxors can be prepared by using appropriate thermal treatments and incorporating small concentrations of B-site (e.g. Zr, Sc and Tb) and A-site (e.g. La) additives.[15-18] The observation of extensive ordered domain growth contradicted the predictions of the space charge model, and instead the B-site order was interpreted using a charge-balanced “random site” model that had been applied previously to the substituted Ba dielectric systems. Additional verification of the random site model was obtained in studies of the Mg/Nb cation distributions using atomic resolution Z-contrast imaging [19] and small angle x-ray scattering [20].

Prior to this new work the space-charge model had also been used to interpret the relaxor properties of PMN; in particular it was assumed that any coarsening of the nano-domains would induce a transition to normal ferroelectric behavior. However, analyses of the dielectric properties of the large domain PMT and PMN ceramics demonstrated that they retain their relaxor response.[15-18] The retention of relaxor type behavior in these systems was suggested to arise from the frustration of long-range ferroelectric coupling by the disorder on one set of positions in the random site structure

This experimental work on PMN has stimulated several new theoretical investigations of the stability of the cation order and its relationship to the ferroelectric properties. For example, the relative importance of the electrostatic interactions between the different B-site cations and the local atomic relaxations of the Pb cations in stabilizing different types of order was explored in references [14,21]. Burton also examined these effects using plane-wave pseudopotential calculations and was able to model the variation in the stability of the cation order in several Pb and Ba 1:2 systems.[22,23] Glazounov, who developed a new “breathing” model for the polarization response, also explored the relationship between the random site model and the relaxor properties.[24]

The complex interplay between B-site cation order and local atomic relaxations is also evident in studies of the influence of pressure and temperature on the ferroelectric behavior of  $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PIN) single crystals.[25] Although partial B-site disorder in PIN was known to induce an antiferroelectric-relaxor transition, in this work pressure was shown to be an important additional parameter in controlling the dielectric response. A transformation to an antiferroelectric phase was observed above 0.4 GPa in crystals with an order parameter ( $S$ ) = 0.4, however specimens with  $S = 0.2$  retained their relaxor behavior up to the highest pressures explored (0.8GPa). The behavior of this system highlights the sensitive balance between the different interactions in the Pb relaxor systems. The competition between anti-ferroelectric and ferroelectric correlations, and the associated role of B-site order/disorder, was utilized by Chen in developing a new model to explain the structural origin of relaxor behavior in a broad range of Pb-based perovskites.[26]

### **A-site ordering in Perovskites: Ionic conduction and Magneto-resistance.**

Compared to the numerous examples of B-site ordered systems, A-site ordered perovskites are relatively rare. Most examples are found in non-stoichiometric, oxygen-deficient perovskites where the ordering of anion vacancies reduces the coordination of some of the A-sites and enhances the driving force for chemical order. The best known example is the  $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$  superconducting system, where the vacancy order produces two different A-site coordination geometries (10 and 8) occupied by the Ba and Y ions respectively. Very few stoichiometric A-site ordered perovskites are known and are typically only found when the A-cations exhibit large differences in valence and size. Park et al., reported on the synthesis and structure of several new stoichiometric A-site systems.[27,28] These new compounds were prepared under high pressure conditions and contained monovalent Ag on the A-sites. While no evidence for A-site order was found in  $(\text{Bi}_{1/2}\text{Ag}_{1/2})\text{TiO}_3$  and  $(\text{Ca}_2\text{NdAg})\text{Ti}_4\text{O}_{12}$ , for  $(\text{Nd}_{1/2}\text{Ag}_{1/2})\text{TiO}_3$   $\text{Nd}^{3+}$  and  $\text{Ag}^+$  were partially ordered in alternating (001) layers. A new modeling scheme was used to assess and predict the stability of A-site order in these and other related systems [28], several of which (e.g.  $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ ) are of interest due to their piezoelectric properties. In this paper it was noted that the stability of the A-site order can be strongly influenced by the chemistry and degree of order on the B-site sub-lattice, this topic was also addressed in a study of A- / B-site order in the  $(\text{Na}_{1/2}\text{La}_{1/2})(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$  system.[29]

A-site order/disorder reactions can play a critical role in affecting the properties of perovskites. Several studies have focused on ionically conducting oxides, for example the Li conducting  $(\text{RE}_{2/3-x}\text{Li}_{3x})\text{TiO}_3$  (RE, rare earth) systems, which are of interest as solid electrolytes in secondary batteries.[30,31] The high mobility of the Li-ions is promoted by significant concentrations of vacant A-sites, but mediated by their degree of order. In the parent Li-free structure ( $x = 0$ ) the A-site cations adopt the usual (001) ordered structure with one layer of vacancies alternating with a second that contains an apparently random distribution of 2/3La and 1/3 vacancies. A-site order is retained in the Li-containing solid solutions, with most of the La cations remaining in one layer and the Li ions and vacancies in the other [32]. Harada et al. studied the effect of bulk composition and degree of A-site order on the magnitude of the Li ion conductivity [30,31]. The ionic conductivities of the disordered A-site samples (prepared by quenching from  $\sim 1150^\circ\text{C}$ ) were approximately an order of magnitude higher ( $\sim 1.5 \times 10^{-3} \text{Scm}^{-1}$ ) than their ordered counterparts ( $\sim 6.8 \times 10^{-4} \text{Scm}^{-1}$ ). The lower conductivity and higher activation energy of the ordered phase was attributed to the decrease in the unit cell volume that

accompanies the ordering transition. Many aspects of the ion distributions in these systems are far from resolved, in particular the degree of short-range order in the mixed (La, Li, vacancy) layers. Using high resolution TEM to study the titanates and the closely related  $(\text{La}_{1/3-x}\text{Li}_{3x})\text{NbO}_3$  niobate system, Alario-Franco and co-workers found evidence for extensive short-range modulations in the Li/vacancy arrangements. [33] They also revealed that the A-site ordering produces multiply twinned nano-domain structures that contain a large volume of domain boundaries. The local chemistry and structure at these boundaries could well play a role in the conduction properties. Following the observation of reduced conduction in the ordered  $(\text{RE}_{2/3-x}\text{Li}_{3x})\text{TiO}_3$  systems, a series of other substitutions have been reported in an effort to maximize the conduction properties. An example of these can be found in reference [34].

A-site order-disorder transitions have also been shown to be effective in mediating the magneto-resistive responses of CMR manganite perovskites. Through extensive studies of a variety of A-site substituted  $(\text{A,A}')\text{MnO}_3$  systems, it is known that for a given charge density the  $T_c$  of the MR transition increases with the average size of the A-site cations. However, a mismatch effect from the size difference of the cations can oppose the increase in  $T_c$  due to local lattice distortions associated with the disorder of the A-site cations. In an elegant study of the  $(\text{LaBa})\text{Mn}_2\text{O}_{6-x}$  system, Millange et al. demonstrated that this effect could be overcome by inducing order on the A-site sub-lattice.[35] In the absence of oxygen vacancies it is difficult to induce long-range La/Ba order and  $(\text{LaBa})\text{Mn}_2\text{O}_6$  adopts a disordered cubic structure. However, by first using reducing conditions to prepare oxygen-deficient  $(\text{LaBa})\text{Mn}_2\text{O}_5$ , long-range La/Ba order (with a doubled c-axis) could be stabilized. By subsequently oxidizing this sample at temperatures low enough to avoid any changes in the A-site distributions, an A-site ordered derivative of  $(\text{LaBa})\text{Mn}_2\text{O}_6$  was obtained for comparison to its corresponding disordered variant. Analysis of the magneto-resistive properties revealed a very large increase in the  $T_c$  from 270K for the disordered polymorph, to 335K for the A-site ordered sample.

### **Mixed Anion Order-disorder.**

The formation of ordered mixed anion solid solutions and compounds offers a novel method for inducing reduced dimensionality in inorganic systems. This area of solid state chemistry has received increased attention and, for example, in the last year several new oxy-fluorides, oxy-nitrides, and oxy-chlorides, have been reported. Only a limited number of

perovskite and  $K_2NiF_4$  related oxy-fluorides were known (e.g.  $BaScO_2F$ ,  $KTiO_2F$ ,  $ANbO_2F$  ( $A = Na, K, Rb$ ),  $Sr_2CuO_2F_2$ ,  $K_2NbO_3F$ ); using fluorination techniques Case et al. [36] were successful in preparing several new iron-based examples. For  $Ba_2InFe(O_5F_{0.68})$ , the first example of an iron oxy-fluoride with a perovskite structure, no evidence was found for (O,F) order. However, in  $Sr_2Fe(O_3F)$  the ordering of F in the apical anion sites of Fe was effective in reducing the dimensionality of the  $K_2NiF_4$ -type structure. Layered oxygen/fluorine order was also observed in a family of  $Sr_3M(O_4F)$  ( $M=Al, Ga$ ) oxides reported in reference [37].

New oxynitrides with  $K_2NiF_4$  and perovskite structures were investigated in reference [38]. Partial order of the anions was observed in  $Sr_2Ta(O_3N)$ , with O's occupying the apical positions and (O/N) statistically distributed in the equatorial positions. Although the controlled synthesis of these mixed anion systems is more difficult than oxide preparations, the additional permutations in stoichiometry, crystal chemistry, and dimensionality offer tremendous potential for interesting new ceramic systems and can be expected to receive increased attention in future years.

### **Ordered Intergrowth Structures.**

The examples of order/disorder cited above involve correlations between individual ions; however, for some systems the substitution of an ion is accommodated by the ordering of different structural slabs. This type of order can generate an homologous series of modulated intergrowth structures. Recent examples include a series of extended defect structures in  $Fe^{3+}$ - and  $In^{3+}$ -substituted ZnO.[39,40] These n-type substituents were explored in an effort to enhance the conductivity of ZnO electrodes for applications in aluminum smelting. The substitution of an  $M^{3+}$  ion into ZnO must be accompanied by structural defects, for example metal vacancies. However, even for quite low concentrations a more stable alternative is to accommodate the aliovalent substituents by forming ordered mixtures of different structural slabs. In the  $In_2O_3$ -ZnO and  $Fe_2O_3$ -ZnO systems the resultant structures are comprised of ZnO-based wurtzite type slabs intergrown with single layers of  $M^{3+}$  in octahedral cavities formed by the close-packed oxygens. A homologous series of compounds  $M^{3+}_2Zn_nO_{3+n}$  were observed with n values ranging from 1 to as high as 48. In addition to characterizing the crystal chemistry of the intergrowth structures, the investigations by high resolution TEM revealed complex modulations in the ZnO slabs and the close packed  $M^{3+}$ -rich layers.[39,40]



Additional examples of this type of intergrowth crystal chemistry can be found in several perovskite-related solid solutions. For example, in the  $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ - $\text{BaZrO}_3$  system the solid solutions were comprised of a homologous series of compounds with alternating blocks of the hexagonal and cubic structural end-members.[41]

## Conclusions.

Examples of cation ordering reactions can be found throughout the inorganic solid state literature. In many cases the degree of order is a critical parameter in controlling and optimizing the property response. For perovskite systems several recent papers have shown that changes in the correlations of the cations on both the A- and B-sites can produce large alterations in dielectric response and conduction properties. Many advances have also been made in first principles calculation of the stability of cation ordering schemes; in the future it can be expected that these successes will be expanded to theory-led design of new systems. An increasing number of ordered anion systems are being discovered, this area also appears to be promising for new materials development.

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