SOME ASPECTS OF DEFECT CHEMISTRY IN P-TYPE PEROVSKITE CONDUCTORS

Xiao-Dong Zhou and Harlan U. Anderson
Electronic Materials Applied Research Center, Department of Ceramic Engineering
University of Missouri-Rolla, Rolla, MO 65401, USA

ABSTRACT

This paper is aimed at addressing some fundamental aspects of defect chemistry in p-type perovskite conductors, including determination of different oxidation states, contribution of various oxidations states to electronic conduction (p type and n type) and magnetic interaction, origin of nonstoichiometry and defect chemistry modeling. Studies on doped and undoped LaMnO$_{3+d}$, LaCrO$_3$, LaFeO$_3$ and La(Ni,Fe)O$_3$ indicate that the electron hole conduction in perovskite mixed ionic-electronic conductors (MIECs) results from high oxidation state of B site cations, in which the electron holes are localized. The magnetic interaction, on the other hand, is attributed to the super exchange between B$^{3+}$ and oxygen ions. The electron conduction in these systems is due to B$^{2+}$; however some of the perovskites can not hold the structural integrity before B$^{2+}$ cations are generated.

INTRODUCTION

Mixed conduction in ceramic oxides is of particular interest because of the simultaneous transport phenomena of ions and electrons (or electron holes). Research on the p type perovskite mixed ionic and electronic conductors (MIECs) has been stimulated by a variety of electrochemical applications during past decades, such as gas separation membranes, fuel cell electrodes, sensors and catalysts. In addition, some of these materials are being considered as candidates for superconductors or components in giant magneto-resistive devices. The most extensive studied materials are the perovskite family oxides with a general formula of ABO$_3$, in which A, the large cation site, may be an alkali, alkaline earth, or rare earth ion, and B, the small cation site, a transition metal cation. The most important unit in the perovskite structure is the BO$_6$ octahedral, which repeats in space to form a large crystal through the fully cornered sharing. The larger cation A will fill the cavity. Since A and B sites are very different in size, the occupancy of these sites is determined primarily by ionic size rather than valency, so it is possible to substitute selectively for either the A or B ion by introducing isovalent or aliovalent cations. The oxygen octahedral is the most important group in perovskites because it can tolerate a variety of local chemical and structural changes, such as distortion, rotation, or redox reaction. This provides a materials scientist an opportunity to alter the properties of a given oxide by choosing hosts and substitutes of either the A or B site to meet the requirements of electrochemical applications by assuming that (i) the electronic conductivity ($\sigma$) is determined by the B site ion; and (ii) the ionic conductivity results from the motion of oxygen vacancies. When a perovskite which
contains transition metal ions on the B site is heated to a sufficiently high temperature that it can equilibrate with the ambient oxygen activity, reversible changes in the oxygen content occur as the oxygen activity is varied. The holes generated through element substitution or changes in oxygen activity are localized on B site cations, thus altering the oxidation states of B site ions. Fluctuation of oxidation states has two primary consequences, (i) influencing the electron-electron interaction between B-O-B, thus magnetic properties, and (ii) influencing the carrier density, thus electrical properties. This paper is aimed at understanding the oxidation states in several typical p type perovskite conductors, including doped LaCrO₃, LaMnO₃, LaFeO₃ and La(Ni,Fe)O₃.

**BASIC DEFECT NOTATIONS AND EQUATIONS**

The occupants at the A site can be $A^\ast_A$, $V_A^-$ and $Sr^\ast_A$ (for simplicity, assume Sr is the lower valence element substituting at the A site). The occupants at the B site are $B^\ast_B$, $B_bB^\ast_B$, and $V_B^-$, where $B^\ast_B$ indicates a majority of B cations are in valence of 3+, $B_b$ represents that some B site cations are in 2+ state and $B'$ shows some B site cations are in 4+ valence state. The oxygen site can have two types of occupants, $V_0^-$ and $O_0^\ast$. Nine equations plus the electron neutrality expression are therefore needed in order to determine these nine defect concentrations. The simple solution which was previously presented (1) in the literature solved for the defect concentrations by restricting the electron neutrality conditions to specific oxygen activity and temperature regimes. This limitation can be removed by making digital solutions to yield the defect concentrations using an electron neutrality expression, which covers the entire oxygen activity and temperature range. Moreover, the universal solution can be obtained independent of chemical composition. Details have been published elsewhere (2-4).

**OXIDATION STATES**

The accuracy for determination of oxidation states and nonstoichiometry lies at the heart in understanding the defect chemistry (4). Exact oxygen occupancy and valence state of B site cation are key parameters that allow a possibility to develop the right defect chemistry model and then to tailor the materials properties.

**LaCrO₃ and LaFeO₃**

Oxidation states in Fe containing systems (Ferrites) are particularly preferable for the use of Mössbauer spectrometry because of the immediate availability of isotope sources, $^{57}$Co, which also can reveal information on chemical bonding and magnetic properties of the ferrites (5). The isomer shift of Mössbauer spectra provides unequivocal information on the oxidation states of Fe ions. The average isomer shift and hyperfine field values were used to study the valence states and hyperfine interaction in these compounds, from which the average Fe valence was achieved for each specimen. In addition, neutron diffraction is a powerful tool to characterize these oxides because it resolves not only the crystal structure, but also the magnetic properties and the oxygen vacancy concentration. Compared to x-ray diffraction, neutron diffraction possesses
several significant advantages, including: (i) the sensitivity of neutron scattering to light atoms such as oxygen is far greater than that of x-ray scattering because the coherent scattering of neutrons is only determined by the nucleus and is independent of the number of electrons and (ii) the neutron has a magnetic moment so it can probe the magnetic structures and excitations through a strong interaction.

Based on the charge neutrality, the oxygen occupancy (3-δ) can be calculated from the oxidation states of the cations, which is plotted in Figure 1 as a function of quenching temperature for Lao.6oSr0.40FeO3-δ. A datum of ~3 for the specimen without quenching is shown in Figure 1 as well. The relative ratio of Fe3+ and Fe4+ ions for Lao.6oSr0.40FeO3-δ without quenching obtained from relative areas of the Mössbauer spectra is 64:36, indicating a nearly zero oxygen vacancy concentration in these compounds. This ratio changes to 70:30 for the specimen quenched from 800°C, showing an increase of oxygen vacancy concentration. Shown in Figure 1 also includes oxygen content, which was directly determined from refinements of neutron diffraction results. A value around 2.8 was observed for Lao.6oSr0.40FeO3-δ quenched from 1500°C, whereas full stoichiometry (δ ~ 0) was determined for Lao.6oSr0.40FeO3-δ without quenching. From charge neutrality, it is evident that Fe is in the valence state of 3+ for Lao.6oSr0.40FeO3.8 and exhibits an average valence state of 3.4 for Lao.6oSr0.40FeO3.0. Therefore, the magnetic moments for Lao.6oSr0.40FeO3-δ are expected to be a function of δ. The magnetic moment and oxygen content can be determined independently by Rietveld refinement of neutron diffraction data. A strong correlation between oxygen deficiency and magnetic moment has been observed, which indicates that this technique can be used to resolve the oxygen content in perovskite type ferrites. In this study, the highest deficiency (δ = 0.2) corresponds to a nearly pure Fe3+ state with a stoichiometric (δ = 0) composition, the fraction Fe3+ is 60% and that of Fe4+ is 40%. The magnetic moment for Lao.6oSr0.40FeO3.8 is ~ 3.8 μB, which is a typical moment for Fe3+ in LaFeO3 system. The magnetic moment for Lao.6oSr0.40FeO3.0 is ~ 2.3 μB (~ 3.8 μB x 60%). The magnetic moment is as expected, linear with vacancy concentration and can be used to determine oxygen content by direct crystallographic refinement. The use of the magnetic moment as a measure of the vacancy concentration has the advantage that it is

![Figure 1. 3-δ vs. quenching temperature for LSF, determined from Mössbauer measurements and refinement of neutron diffraction.](image-url)
quite precise and the uncertainty in magnetic moment is 2% at low vacancy concentration, decreasing to less than 1% when the moment is large.

Questions still remain as to the behavior of electrons in Fe$^{4+}$ ions. Information on multivalent Fe site cations and valency distribution can contribute to understanding conduction mechanisms in p type perovskite family oxides. At high temperatures, LSF will lose oxygen to form oxygen vacancies, at the cost of decreasing hole concentration. This reaction can be represented in Kroger-Vink notations:

$$2\text{Fe}^{*}_{\text{Fe}} + \text{O}_2^* \rightarrow \frac{1}{2} \text{O}_2 + 2\text{Fe}^{*}_{\text{Fe}} + \text{V}^{**},$$

where Fe$^{*}_{\text{Fe}}$ represents Fe ions in the 4+ valence state (similar to holes), Fe$^{*}_{\text{Fe}}$ indicates Fe cations in 3+, and V$^{**}$ represents the oxygen vacancy. Thus, the hole conductivity ($\sigma$) follows $\sigma = N \mu q$, where $\mu$ is the mobility, $q$ is the carrier charge and $N$ is the hole concentration (Fe$^{4+}$). Because of the much higher mobility of the electrons or holes than that of oxygen ions, the total conductivity in ferrites is dominated by hole conduction. The carrier concentration can be directly determined from the measurements of Seebeck coefficient ($Q$). Figure 2 shows the plots of carrier density calculated from Fe$^{4+}$ concentration, which is determined from the Seebeck coefficient and Fe$^{4+}$ fraction in the system.

![Figure 2. A plot of carrier density calculated from Fe$^{4+}$ concentration and measured carrier density from Seebeck coefficient (Q).](image)

One would expect that a p-n transition occurs when the Fe$^{*}_{\text{Fe}}$ concentration (functioning as holes) further decreases, and the average Fe valence drops below 3+, generating electron carriers. Theoretically, both increasing temperature and decreasing oxygen activity can drive this transition. However, resistivity measurements at 1600°C are extremely difficult to perform. Therefore, we studied this phenomenon by decreasing oxygen activity (from $10^{-13}$ Pa to $10^{-5}$ Pa) at 1000°C. Figure 3 illustrates this transition. In the $p\text{O}_2$ region from $10^{-9}$ Pa to $10^{-5}$ Pa, the total isothermal conductivity decreases due to decrease of Fe$^{*}_{\text{Fe}}$ (hole) concentration as a result of generation of oxygen vacancies.
At the minimum conductivity, Mössbauer data on quenched samples show nearly all Fe cations are in 3+ valence state and oxygen occupancy ~ 2.8, in agreement with the neutron results. Further decreasing oxygen activity increases the Fe$^{2+}$ concentration, which functions as electrons. Thus, conductivity (n type) increases when pO$_2$ < 10$^{-9}$ Pa (shown in Figure 3).

![Figure 3. A p-n transition in LSF due to changing of oxygen activity (6).](image)

Difficulties exist in directly determining the oxidation states of Cr ions in chromites, however, extensive work has been performed to indirectly study the Cr oxidation states in A site and/or B site doped (La,Y)CrO$_3$. For example, Flandermeyer et al. (7) showed that the existence of Cr$^{4+}$ in La(Mg,Cr)O$_3$, from which the conductivity and oxygen nonstoichiometry could be fit with a simplified defect chemistry model quite well.

**(La,A)MnO$_3$ (where A = Sr or Ca)**

Oxidation states of Mn ions in manganites are far more complicated than those of chromites or ferrites. The reasons may have two aspects; (i) manganites often have oxygen excess, and (ii) carrier density is anomalously high in undoped LaMnO$_3$. These two reasons may be correlated. An extensive study was done in the early 1990s by Raffaelle et al. (8,9), who designed a unique compound as La$_{1-x}$Sr$_x$Cr$_{1-y}$Mn$_y$O$_{3+x}$ (x = 0 and 0.1; 0 ≤ y ≤ 1.0). A nearly constant carrier density was observed at T > 1000°C when the Mn fraction was higher than 60%, which seemed to be independent of either Sr dopant or Mn contents. They argued that the lack of change in carrier density was due to charge disproportionation from Mn$^{3+}$ to Mn$^{2+}$ and Mn$^{4+}$, which preserved Mn$^{4+}$ density through the conversion of Mn$^{2+}$ to Mn$^{3+}$. Additionally, the charge disproportionation reaction successfully explained the carrier density at low Mn concentration through a so-called “trapping to percolation” theory. The charge disproportionation reaction may be very trivial, if there exists, in ferrite systems, as aforementioned magnetic discussion. Mizusaki et al. (10) recently reported that p type conduction changed to n type in the system of La$_{1-x}$Sr$_x$MnO$_{3+x}$ when x > 0.5, which was deduced from Seebeck coefficient with a value close to zero for x = 0.5 and less than...
zero for $x = 0.7$. Complexity in manganites necessitates similar studies on coupled magnetic and electrical properties.

**La(Ni,Fe)O$_3$**

The Fe$^{4+}$ was argued to be favorable in La(Ni$_{1-x}$Fe$_x$)O$_3$, based on the Goodenough-Kanamori super exchange rules, when Ni content ($x$) is small (<0.5) (11). Mössbauer measurements were performed by Goeta et al. (3) on $x = 0.25$. They obtained Fe$^{4+}$ to Fe$^{3+}$ populations as 52(3)% and 48(3)%, which indicates that a large fraction of Ni cations (~52%) have been pushed from Ni$^{3+}$ to Ni$^{2+}$. The anomalous Fe$^{4+}$ density leads us to postulate that the carrier density is very high in La(Ni,Fe)O$_3$, in particular when $x > 0.5$. Electrical conductivity measurements were performed on the sintered bars of $x = 0.4$.

![Figure 4. A plot of $\sigma$ vs. temperature for LNF measured in air.](image)

Figure 4 shows the plots of $\sigma$ vs. temperature (°C) for LNF measured in air from 200°C to 1200°C. A maximum conductivity around 250°C was observed for all gas atmospheres with $\sigma \sim 540$ S/cm in air. A maximum conductivity has been observed in many p-type conductors, which was explained from defect chemistry analysis. The electroneutrality condition is given in the Kröger-Vink notation as $[A_{Fe}^{\cdot}] = 2[V_{O}^{\circ}] + [h^{\circ}]$, where $[A_{Fe}^{\cdot}]$ is the acceptor dopant concentration, $[V_{O}^{\circ}]$ is the oxygen vacancy concentration and $[h^{\circ}]$ is the hole concentration. The oxygen vacancies are generated at high temperature due to loss of oxygen, which results in a higher $[V_{O}^{\circ}]$ and a lower $[h^{\circ}]$, assuming $[A_{Fe}^{\cdot}]$ is constant. Therefore, since $\sigma = \mu n q$, where $n$ is the carrier concentration and $q$ is the carrier charge, at elevated temperature, the mobility increases whereas the carrier concentration, $n$, decreases, which results in the maximum conductivity. This was found to be valid in most of A site substituted ferrites, manganites and chromites, such as La$_{1-x}$Sr$_x$FeO$_3$, La$_{1-x}$Sr$_x$MnO$_3$ and La$_{1-x}$Sr$_x$CrO$_3$. Both the thermogravimetric analysis and refinements of neutron diffraction showed that oxygen vacancy density was around 1% for LNF quenched from 1100°C, therefore the decrease in conductivity at $T > 1100$°C in Figure 4 can be contributed to generation of oxygen vacancies. Oxygen content in LNF, however, was determined to be ~3.0 for the
sample quenched from $T < 1000^\circ$C. Thus, the decreasing conductivity in LNF from 300 to 1000$^\circ$C may not be attributed to generation of oxygen vacancies. This behavior is not well understood. Chainani et al. (3) has studied low temperature electrical conductivity of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ and observed an increase of conductivity in the temperature range from 2 to 300 K for $x > 0.3$. They explained this behavior in terms of a metal-insulator transition and therefore, the negative temperature coefficient for conductivity was the result of scattering. This explanation seems reasonable, however, the conductivity value in their system was much lower (~10X) than that measured in this study, which could be because the sintering temperature (800$^\circ$C) was too low and thus the final density was too low and the specimens were porous.

![Figure 5. A plot of $\ln(\sigma T)$ vs. $1/T$ for LNF measured in air.](image)

A plot of $\ln(\sigma T)$ vs. $1/T$ (Figure 5) may enable us to understand the conduction mechanism by assuming a small polaron conduction in LNF system and mobility following non-adiabatic condition as $\mu \propto \frac{n_0}{T} \exp\left(-\frac{E_a}{kT}\right)$. A maximum of $\ln(\sigma T)$ was observed at $T = 1000^\circ$C, at which oxygen vacancies started to play a role in the total carrier concentration. Two separate regions at $T < 1000^\circ$C with activation of 0.06 eV and 0.04 eV indicate the possibility of different conduction mechanisms for temperature less than 1000$^\circ$C. A comparison of LNF with LSF, LSM and LSCr suggests that the LNF redox reaction takes place in two cations, Ni and Fe, whereas the redox reaction only occurs for a single cation in LSF, LSM and LSCr system. This may be the reason that the nonlinearity is observed. The very low activation energy may very well represent small polaron conduction; however more work has to be performed in order to resolve the conduction mechanism.

CONCLUSIONS

Oxidation states of the B site ions in p type perovskite conductors have been discussed in ferrites, chromites, manganites and nickelates. The low valence element substitution

Electrochemical Society Proceedings Volume 2005-07

1485

Downloaded on 2019-04-27 to IP 207.241.231.83 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).
into ferrites and chromites was compensated by higher oxidation state Fe and Cr, both in 4+ states. Charge disproportionation was assumed in manganites, which successfully explained the origin of higher carrier density in undoped LaMnO$_{3+y}$. The disproportionation reaction is trivial in LaFeO$_3$ and LaCrO$_3$ systems. A large fraction of high oxidation Fe ions (4+) was observed in the La(Ni,Fe)O$_3$ system. Complexity of oxidation states in manganites and nickelates necessitates further studies on coupled electrical and magnetic properties.

ACKNOWLEDGEMENTS

The authors wish to thank the Department of Energy, the Gas Research Institute and Praxair, Inc who provided financial support for part of this research.

REFERENCES

1. H. U. Anderson, Solid State Ionics, 52, 33-41 (1992).
2. J. Nowotny and M. Rekas, J. Am. Ceram. Soc., 81, 67-80 (1998).
3. F. W. Poulsen, Solid State Ionics, 129, 145-162 (2000).
4. X.-D. Zhou and H. U. Anderson, in Materials for Energy Conversion Devices, C. C. Sorrell, J. Nowotny, and S. Sugihara, Eds., Woodhead Publishing Ltd., (2004), in press.
5. X.-D Zhou, Q. Cai, Z. Chu, J. Yang, W. B. Yelon, W. J. James and H. U. Anderson, Solid State Ionics, 175, 83-86 (2004).
6. X.-D. Zhou, J. B. Yang, Q. Cai, M. Kim, W. B. Yelon, W. J. James and H. U. Anderson, J. Appl. Phys., in press.
7. B. K. Flandermeyer, “Thermogravimetric and Electrical Conductivity Studies of Mg-doped LaCrO$_3$ and La Doped SrTiO$_3$,” University of Missouri-Rolla, Dissertation, (1984).
8. R. Raffaelle, H. U. Anderson, D. M. Sparlin, and P. E. Parris, Phys. Rev. B, 43, 7991-7999 (1991).
9. R. Raffaelle, H. U. Anderson, D. M. Sparlin, and P. E. Parris, Phys. Rev. Lett., 65, 1383-1386 (1990).
10. J. Mizusaki, Y. Yonemura, H. Kamata, K. Ohyama, N. Mori, H. Takai, H. Tagawa, M. Dokiya, K. Naraya, T. Sasamoto, H. Inaba, and T. Hashimoto, Solid State Ionics, 132, 167-180 (2000).
11. N. Y. Vasanthacharya, P. Ganguly, and C. N. R. Rao, J. Solid state Chem., 53, 140-143 (1984).
12. A. E. Goeta, G. F. Goya, R. C. Mercader, and G. Punte, Hyperfine Interactions, 90, 371-375 (1994)
13. A. Chainani, D. D. Sarmayk, I. Dasz and E. V. Sampathkumaranz, J. Phys. Cond. Matt., 8, L631-L636 (1996).