Journal of Solid State Chemistry 198 (2013) 407–415

Contents lists available at SciVerse ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Local structures of Sr_2FeMnO_{5+y} ($y=0$, 0.5) and $Sr_2Fe_{1.5}Cr_{0.5}O_5$ from reverse Monte Carlo modeling of pair distribution function data and implications for magnetic order

Graham King [a],*, Farshid Ramezanipour [b], Anna Llobet [a], John E. Greedan [b]

[a] Lujan Neutron Scattering Center, Los Alamos National Laboratory, MS H805, Los Alamos, NM 87545, USA
[b] Department of Chemistry and Brockhouse Institute for Materials Research, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada L8S 4M1

ARTICLE INFO

Article history:
Received 24 July 2012
Received in revised form
31 October 2012
Accepted 4 November 2012
Available online 13 November 2012

Keywords:
Perovskite
Brownmillerite
Oxygen deficient
Pair distribution function
Local structure
Reverse Monte Carlo

ABSTRACT

The local structures of the oxygen deficient perovskites Sr_2FeMnO_5, $Sr_2FeMnO_{5.5}$, and $Sr_2Fe_{1.5}Cr_{0.5}O_5$ have been analyzed using neutron pair distribution function data. The results show that locally all three structures are more complex than implied by their average cubic structures and that the distributions of oxygen vacancies are not completely random on a local level. For both Sr_2FeMnO_{5+y} compounds it is found that there is no short range ordering of the Fe and Mn cations. For $Sr_2Fe_{1.5}Cr_{0.5}O_5$ there is evidence to suggest that the Fe/Cr distribution is not completely random and is locally ordered such that there are fewer Fe–Fe nearest neighbor pairs than in a random distribution. Reverse Monte Carlo modeling of the pair distribution function data has provided the Fe–O, Mn–O, and Cr–O bond length distributions and information on the coordination numbers of the Fe, Mn, and Cr cations. In Sr_2FeMnO_5 it is found that the Fe^{3+} cations are most often in 4-fold coordination but there is also a large amount of Fe^{3+} in 5-fold coordination and a small amount in 6-fold coordination. The Mn^{3+} is split between 5-fold and 6-fold coordination. The Mn–O bond length distributions indicate that the $Mn^{3+}O_6$ octahedra and $Mn^{3+}O_5$ square pyramids are locally Jahn–Teller distorted. In $Sr_2FeMnO_{5.5}$ the Fe^{3+} is almost entirely 5 coordinate while the Mn^{4+} is almost entirely 6 coordinate. The Cr^{3+} in $Sr_2Fe_{1.5}Cr_{0.5}O_5$ is almost entirely 6-fold coordinated, giving the Fe^{3+} an average coordination number of 4.67. In Sr_2FeMnO_5 and $Sr_2Fe_{1.5}Cr_{0.5}O_5$ the Fe^{3+} and Sr^{2+} cations undergo local displacements which are driven by the oxygen vacancies, while the Mn^{3+} and Cr^{3+} cations remain near their positions in the average structures. In $Sr_2FeMnO_{5.5}$ these cations are not significantly displaced. The local coordination geometries are used to explain previously observed but yet poorly understood magnetic properties of these materials.

1. Introduction

Oxygen deficient perovskites are of interest for many different applications which include use as ionic conductors [1] and magnetoresistant materials [2]. The structures adopted by oxygen deficient perovskites can vary greatly depending on the concentration of vacancies as well as whether or not the vacancies are ordered. For those compositions with an ordered arrangement of vacancies a variety of possible structures can result. Compositions which lack long range ordering of vacancies usually adopt simple cubic structures, but can have more complex local structures due to short range ordering of the vacancies [3]. Knowing the local structure is essential for understanding the properties, as it is the local structure which determines the ground state energies in the system [4].

The ideal perovskite structure has stoichiometry *ABX*$_3$ and cubic *Pm*-3*m* space group symmetry. In this structure the *B*-site cations are octahedrally coordinated by the *X* anions while the *A*-site cations sit in a 12-fold cubooctahedral site. The structure consists of a three dimensional network of corner sharing *BX*$_6$ octahedra with the *A*-site cations residing in the large voids between any eight such *BX*$_6$ units (Fig. 1). Deviations from the ideal structure are common and can occur for a variety of reasons which include tilting of the *BX*$_6$ octahedra, first or second order Jahn–Teller distortions of either *A* or *B*-site cations, cation ordering, or ordering of *A*-site or anion vacancies [5]. In anion deficient perovskites the ordering of anion vacancies and the ordering of cations are often strongly linked [5,6].

Perovskites with iron or manganese on the *B*-site can both form phases where one-sixth of the anion sites are vacant, although they tend to adopt different structure types. $A_2Fe_2O_5$ compositions tend to adopt brownmillerite structures. In a brownmillerite structure the anion vacancies are ordered in such a way as to create layers

---

* Corresponding author. Fax: +1 505 665 2676.
E-mail address: gking@lanl.gov (G. King).

0022-4596/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jssc.2012.11.005

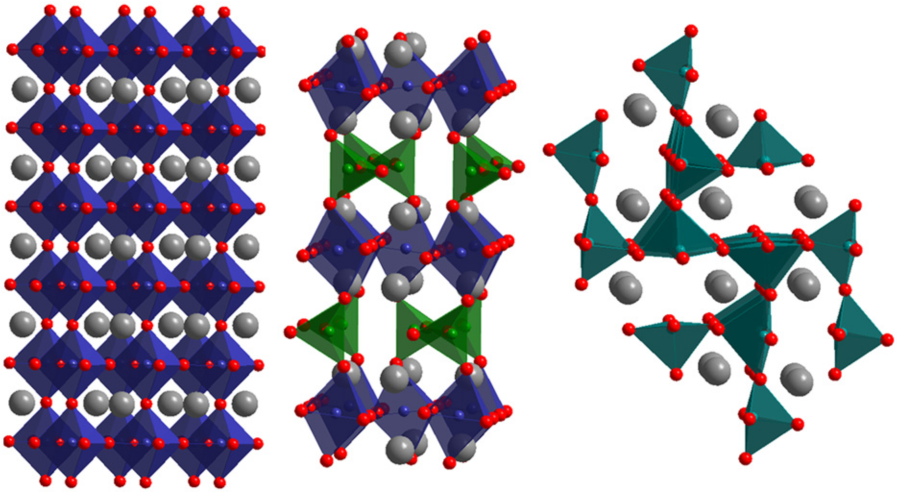

Fig. 1. The structures of the simple cubic perovskite with a random distribution of oxygen vacancies (left, O site 5/6 occupied), the brownmillerite structure with chains of tetrahedra and layers of octahedra (middle, *Ibm*2 variety shown), and the structure of $Sr_2Mn_2O_5$ with all Mn in square pyramidal coordination (right). The small blue, green, or aqua spheres are the *B*-site cations, the large gray spheres are the *A*-site cations, and the red spheres are the oxygen anions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

containing chains of BO_4 tetrahedra which are separated by layers of BO_6 octahedra (Fig. 1). Several different space groups have been found for brownmillerites which depend on the ordering of the tetrahedral chains within and between layers [3]. For Fe containing phases it has been found that the size of the *A*-site cation is strongly correlated with the degree of anion vacancy ordering. For example, $Ca_2Fe_2O_5$ has an ordered orientation of the tetrahedral chains to give *Pnma* space group symmetry, while in $Sr_2Fe_2O_5$ the tetrahedral chain orientations are disordered resulting in *Imma* space group symmetry [7–9]. In contrast, $A_2Mn_2O_5$ compounds tend to adopt a different pattern of vacancy ordering in which all Mn cations have square pyramidal coordination geometry (Fig. 1) [10–12].

Compositions with a mixture of both Fe and Mn on the *B*-site are also known [3,13–15]. For such phases the *A*-site cations also affects the degree of anion ordering, but in an even more dramatic way than for the pure Fe compounds. Ca_2FeMnO_5 is a brownmillerite with well ordered tetrahedral chains (*Pnma*). In this compound there is a strong preference for the Fe to occupy the tetrahedral site and the Mn to occupy the octahedral site, resulting in a layered ordering of these two cations. Replacement of only half the Ca atoms with Sr atoms is sufficient to disorder the chains such that $CaSrFeMnO_5$ has *Imma* space group symmetry and the brownmillerite domains are reduced to the nanoscale [14]. Replacement of all the Ca with Sr to give Sr_2FeMnO_5 results in complete loss of long range anion and cation ordering, giving the simple cubic perovskite structure.

For oxygen deficient perovskites with vacancy concentrations less than 1/6, vacancy ordered phases also exist. For example, $Sr_2Fe_2O_{5.5}$ ($Sr_4Fe_4O_{11}$) with a 1/12 concentration of vacancies and $Sr_2Fe_2O_{2.75}$ ($Sr_8Fe_8O_{23}$) with a 1/24 concentration of vacancies form supercells with a mixture of square pyramidal and octahedral *B*-site cation coordination geometries and symmetries of *Cmmm* and *I*4/*mmm*, respectively [16]. However, in many such compounds there is no long range vacancy ordering and cubic perovskite structures result, such as in the cases of $Sr_2FeMnO_{5.5}$ and $CaSrFe_{1.5}Mn_{0.5}O_{5.5}$ [3,14,16].

There have also been some recent studies involving oxygen deficient perovskites with Fe and Cr on the *B*-site [15,17,18]. For these compounds it is again observed that smaller *A*-site cations lead to vacancy ordering while larger *A*-site cations lead to disordered cubic structures. For example, $Ca_2Fe_{1.5}Cr_{0.5}O_5$ is a brownmillerite while $Sr_2Fe_{1.5}Cr_{0.5}O_5$ is cubic. One particularly interesting property of $Sr_2Fe_{1.5}Cr_{0.5}O_5$ is that this compound shows long range magnetic order well above room temperature despite not having any long range ordering of the vacancies or the Fe^{3+}/Cr^{3+} cations [17]. This is quite different than the spin glass like behavior observed for most compounds which have a disordered arrangement of magnetic cations. For example, Sr_2FeMnO_5 and $Sr_2FeMnO_{5.5}$ do not show any long range magnetic ordering but instead display short range ordering below 50 and 25 K, respectively [3].

This study is concerned with the local structures of oxygen deficient perovskites which have simple cubic perovskite average structures. Preliminary analysis of the pair distribution functions (PDFs) of Sr_2FeMnO_5 and $Sr_2Fe_{1.5}Cr_{0.5}O_5$ has been carried out before [3,17]. These studies found that the average cubic models could not adequately fit the low *r* regions of the PDFs and that brownmillerite models were able to provide better fits. However, these fits were still not completely satisfactory, particularly in the case of Sr_2FeMnO_5. The local structure of $Sr_2FeMnO_{5.5}$ has not been studied by PDF analysis before. In this study the "large box" Reverse Monte Carlo (RMC) method is used to perform the first ever study of the local structure of $Sr_2FeMnO_{5.5}$ as well a more detailed analysis of the local structures of Sr_2FeMnO_5 and $Sr_2Fe_{1.5}Cr_{0.5}O_5$. The RMC method uses large supercells containing $\sim 10^4$ atoms which are adjusted to fit the experimental data. This method is highly flexible and is able to model more complex local structures than is possible using traditional "small box" methods. The RMC method is often able to provide details of the local structure that cannot be obtained by more conventional analysis. It also has the advantage of being able to model the short, medium, and long range structural features simultaneously with a single model. This method has been previously used to separate out the local coordination environments of two *B*-site cations disordered over a single site in other perovskite systems [19]. One additional goal of this study is to explain the very different long range magnetic ordering behavior observed in these compounds by correlating the magnetism with the features of the local structures.

2. Experimental

The synthesis of these compounds has been reported previously [3,17]. Neutron total scattering data was collected for all samples at the Lujan Neutron Scattering Center at Los Alamos National Laboratory. Data for Sr_2FeMnO_5 and $Sr_2Fe_{1.5}Cr_{0.5}O_5$ was