Identifying the Local Structural Units in $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ and $\text{BaY}_{0.25}\text{Fe}_{0.75}\text{O}_{2.5}$ through the Neutron Pair Distribution Function

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Abstract

Neutron pair distribution function data are used to investigate the local structures of two oxygen deficient perovskites with simple cubic crystal structures. $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ is found to have alternating layers of MnO_6 octahedra and MnO_4 tetrahedra, making it similar to other members of the $\text{La}_{1-x}\text{Ba}_x\text{MnO}_{2.5}$ series with smaller x values which have brownmillerite crystal structures. Our fitting results suggest that $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ is not locally similar to any one brownmillerite structure type but instead has a variety of intra-layer and inter-layer relationships. We propose that this could be due to short range segregation of the much differently sized La^{3+} and Ba^{2+} cations, which creates significantly different inter-layer distances. $\text{BaY}_{0.25}\text{Fe}_{0.75}\text{O}_{2.5}$ is found not to have a brownmillerite-type local structure but rather seems to consist of structural units which are similar to $\text{Ba}_3\text{YFe}_2\text{O}_{7.5}$, and earlier member of the $\text{Ba}_n\text{YFe}_{n-1}\text{O}_{2.5n}$ series. The PDF analysis shows that there are never neighboring Y atoms and that the O vacancies lie exclusively between Fe atoms, such that Y is always octahedrally coordinated. The PDF also suggests that there are more tetrahedral Fe than expected, which could be due to the presence of terminal O atoms in Fe centered dimeric units, similar to what is found in $\text{Ba}_3\text{YFe}_2\text{O}_{7.5}$.

1. Introduction

Complex transition metal oxides have garnered a lot of attention due to their structural complexity and attractive physical properties. Perovskites containing oxygen vacancies are one such class of materials which have been investigated for a number of different applications, such as ionic conductors. There are a large number of different structure types that can be derived from the perovskite structure by having an ordered arrangement of the vacancies. These structure types often involve cation ordering which is synergistic with the vacancy ordering and they can be quite complex.¹ On the other hand, there are also oxygen deficient perovskites which lack any long range cation or anion vacancy ordering and adopt simple cubic crystal structures. However, several recent studies have shown that such compounds can have a large degree of short range order such that the local structure is very different from the average long range structure.²⁻⁷

This study looks at the local structures of two such compounds, $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ and $\text{BaY}_{0.25}\text{Fe}_{0.75}\text{O}_{2.5}$. While both compounds have simple cubic perovskite structures, our neutron pair distribution function (PDF) data show that locally they both contain a large amount of short range order. By comparing their local structures with the crystal structures of related compositions we gain an understanding into what structural units these materials are comprised of and how they fit into known series of compounds.

2. Experimental

The $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ compound was prepared by the topotactic reduction of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ in a similar manner as has been reported for related compositions.⁸ $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ was prepared via a citrate gel method. The appropriate stoichiometric ratios of La_2O_3 (99.999 %, dried at 900 °C), BaCO_3 (99.997 %), and MnO_2 (99.999 %) were dissolved in a minimum quantity of 6M nitric acid. Two molar equivalents of citric acid and 5 mL of analar ethylene glycol were added and the solutions heated with constant stirring. The gels thus formed were subsequently ground into a fine powder, placed in an alumina crucible, and heated at 1 °C min⁻¹ to 900 °C in air. The powders were then ground again and pressed into 13 mm pellets under a force of 5 tonnes. Samples were then heated under flowing argon at 1500 °C for two periods of 24 h. After being cooled, the pellets were reground and the resulting powders heated in an alumina boat at 400 °C under flowing oxygen for 12 hours to achieve full oxygen stoichiometry. The formation of a single phase sample of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ was confirmed by X-ray powder diffraction.

Reduction of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ to $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ was achieved using sodium hydride as a reducing agent. $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ was combined with a double-stoichiometric quantity of NaH in an argon-filled glove box. The resulting mixture was then sealed under vacuum in a Pyrex tube and heated for 1 day at 200 °C and then at 210 °C for a further day. The sample was then reground and heated for 2 days at 215 °C and, after a further grinding, at 220 °C for 2 more days.

The sample was then washed under nitrogen with 4×100 mL of methanol to remove sodium containing phases (NaOH and NaH) before being dried under a vacuum.

The synthesis of $\text{BaY}_{0.25}\text{Fe}_{0.75}\text{O}_{2.5}$ has already been reported in a previous paper.⁹

Neutron total scattering data for both compounds were collected at 300 K on the NPDF instrument at the Lujan Neutron Scattering Center of Los Alamos National Laboratory. Rietveld refinements to determine the average crystal structures were done using the GSAS/EXPGUI programs.^{10,11} The reduction and merging of the neutron data to obtain the pair distribution function, $G(r)$, was done using the PDFgetN program with a Q_{max} of $30 \text{ \AA}^{-1}$. The data from banks 3 and 4 was used up to $30 \text{ \AA}^{-1}$ while the data from banks 1 and 2 were cutoff at 10 and $20 \text{ \AA}^{-1}$, respectively. The small box fitting of the $G(r)$ was done using the program PDFgui while the RMC modeling was done using the program RMCProfile.^{12,13}

3. Results and Discussion

3.1 Average Structures. Rietveld refinements of the neutron powder diffraction patterns confirm that both compounds have the basic cubic perovskite structure with no long range ordering of cations or anion vacancies. The structural parameters from the fits are given in Table 1. The unit cell parameters, isotropic atomic displacement parameters (ADPs), and site occupancies were refined. The site occupancies all refined to be fairly close to the expected values while the ADPs were quite large, which can be indicative of local displacements. There was a rather strong correlation between the site occupancies and ADPs, as is typical in Rietveld refinements. The values shown in Table 1 are the ADPs obtained when the site occupancies were fixed to their nominal values. The fits are shown in Figures S1 and S2 of the supporting information.

3.2 Local Structure of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$. The neutron PDF of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ was initially fit using the average cubic structure determined from Rietveld refinement as a model. Refinements were done over a variety of r -ranges. Parameters obtained from some of the fits are given in Table 2. The fit at low r , below $\sim 3.5 \text{ \AA}$, is quite poor (Fig. 1). The first peak, which corresponds to the nearest neighbor Mn–O distances (this peak is negative owing to the negative neutron scattering length of Mn) and the second peak, which corresponds to nearest neighbor A–O and O–O distances, have complex shapes that cannot be accounted for by a cubic model. At medium r ranges the fit was not as poor but there were still significant discrepancies between the data and the model (Fig. S3). At higher r , above $\sim 14.5 \text{ \AA}$, the model provides a fairly good fit, although there were still minor issues and the thermal parameter for the O atom still refined to an unrealistically large value (Fig. S4). This confirms that there are large local deviations from the average structure and a large amount of short range order is present.

There are several possibilities for what the local structure of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ could look like. A cation and vacancy ordered version of this compound is known which has a layered ordering of La and Ba and all Mn cations in square pyramidal coordination (Fig. S5).¹⁴ The

cation ordered structure, $\text{LaBaMn}_2\text{O}_5$, is the thermodynamic version while the disordered $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ represents a meta-stable form obtained using the low temperature topotactic method described above. The $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ compound can also be considered a member of the $\text{La}_{1-x}\text{Ba}_x\text{MnO}_{2.5}$ series of compounds. For this series members with small values of x adopt brownmillerite (BM) structures which have alternating layers of octahedrally and tetrahedrally coordinated Mn cations. It could also be that the structure has significant amounts of Mn with coordination numbers of 4, 5, and 6. Such a structure could have a fully random distribution of La/Ba but have the vacancies preferentially occurring around the smaller La cations.

Determining the coordination environment of Mn is difficult since for all models the average coordination number is 5, therefore the intensity of the Mn–O peak is the same for all models. It is also complicated since the oxidation state of Mn is non-integer at 2.5, making it difficult to predict the expected bond lengths for certain situations. Since the $\text{BaLaMn}_2\text{O}_5$ compound does not charge order until well below room temperature the Mn in $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ are probably best described as all being $\text{Mn}^{2.5+}$ rather than having distinct Mn^{2+} and Mn^{3+} . Something can be said about the coordination number of Mn by looking at the shape of the Mn–O peak. As can be seen in Figure 1, the Mn–O peak has its maximum at 2.02 Å but then has a shoulder at ~2.16 Å. In the RT crystal structure of $\text{LaBaMn}_2\text{O}_5$ the Mn–O bond lengths have a narrow distribution, with 4 bonds at 2.00 Å and 1 bond at 2.05 Å. In contrast a BM structure would be expected to have a much broader distribution of bond lengths. Mn–O bonds around 2.16 Å could only be expected from octahedrally coordinated Mn such as would be present in a BM structure. The PDF was fit using the crystal structure of $\text{LaBaMn}_2\text{O}_5$ as a model. Several fits were also done using various BM structures as models. The fits using $\text{LaBaMn}_2\text{O}_5$ were unable to model the shape of the Mn–O peak (Fig. S6). However, all of the BM models were able to account for the shape of this peak. The BM models also provided better fits to the next several peaks in the PDF as well. This analysis shows that the Mn coordination environment is best described as consisting mostly of tetrahedral and octahedral, although the presences of some 5 coordinate Mn cannot be excluded.

Brownmillerite structures can be derived from the perovskite structure by removing oxygen atoms from every other BO_2 layer, in an ordered manner, such that there are layers of BO_4 tetrahedra alternating with layers of BO_6 octahedra. Different BM structure types arise because the chains of tetrahedra can twist either clockwise or counterclockwise. If all chains in the structure are twisted in the same direction a polar structure with $I2mb$ symmetry results. Such structures are thought to occur when the twist, and therefore the dipole moment, of the chains is small. If all the chains in a layer twist in the same direction but the direction of the twist alternates between layers then a non-polar structure with space group $Pnma$ results. Such structures occur for intermediate magnitudes of the dipole moment. It is also possible to have two unique types of chains of opposite twist within a layer of tetrahedra. This can lead to additional structure types depending on how these layers are stacked relative to each other. If the layers are the same, an AAAA... type stacking, then $C2/c$ symmetry results. If the layers alternate with an ABAB... pattern then the structure has $Pcmb$ symmetry. Parsons et al. have

made a predictive chart based on known examples and rationalized the structures in terms of a competition between dipole cancellation and distortions of the intervening octahedral layers.⁸ The $\text{LaBaMn}_2\text{O}_5$ composition falls within the ordered intra-layer region of the diagram in reference 8, which would seem to suggest that $C2/c$ or $Pcmb$ are the more likely structures. However, for members of the $\text{La}_{1-x}\text{Ba}_x\text{MnO}_{2.5}$ series with x less than 0.5 $C2/c$ and $I2mb$ structures are found, which could suggest that the local structure might be $I2mb$ as well.

The PDF of $\text{LaBaMn}_2\text{O}_5$ was fit with 4 different models over a large variety of r -ranges using the small box PDFgui software (Table 3). The models had $I2mb$, $Pnma$, $C2/c$, and $Pcmb$ symmetry and were adopted from known examples of BM compounds which have these structures. All models could produce reasonably good fits if the refinements were done only over low r -space (Fig S7). This is because all models have similar coordination environments for the ions. The differences between the structures arise due to differences in intra-layer chain ordering and/or inter-layer chain ordering, which do not affect the first few peaks in the PDF very much. Good fits could also be obtained with any of the models if done over a narrow range of r -space, such as from only 6-12 Å, probably owing to the large number of atomic degrees of freedom in these structures. However, none of the models were able to produce a fully satisfactory fit when the refinement was done over a wide range of r -space, especially if the fits included the low- r region (Fig. S8). Furthermore, the structural parameters obtained from fitting one r -range could not account for the PDF of a different r -range. Overall the $I2mb$ model provided the worst fit, the $Pnma$ model the next best, and the $Pcmb$ and $C2/c$ models similar fits which were superior to the other two models. The $Pcmb$ model tended to fit well at low- r while the $C2/c$ model became better at higher- r . The PDF was also fit using the large box RMC method using starting models with the $Pcmb$ and $C2/c$ structures. Despite the flexibility of this method the RMC fits using either of these models were not completely satisfactory. Both models were able to provide an excellent fit to the low- r region of the PDF but neither was able to fit well the data above ~6 Å in r -space. This shows that the local structure is indeed brownmillerite-like, but that the relationship between layers is not identical to any of the known BM structure types.

The fitting results show that the local structure of $\text{LaBaMn}_2\text{O}_5$ cannot be described as being simply analogous to any known BM crystal structure. The most likely reason for this is that there are a variety of local structures present. In order to understand the origin of this variety it is worthwhile to consider why the $\text{La}_{1-x}\text{Ba}_x\text{MnO}_{2.5}$ series exhibits different behavior than the analogous Sr or Ca series. These two series have $C2/c$ structures for small values of x which transition to $Pcmb$ structures for larger values of x . The Ba series has $I2mb$ structures which transition to $C2/c$. The Ba series also transitions to a disordered cubic structure at a significantly lower x value than for the other two series.⁸ One factor that was not considered in previous work is the size mismatch between the two A-site cations. The 8 coordinate ionic radius of La^{3+} (1.16 Å) falls between that of Ca^{2+} (1.12 Å) and Sr^{2+} (1.26 Å). As such, having a disordered arrangement of La/Ca or La/Sr on the A-sites causes minimal strain. In contrast, the ionic radius of Ba^{2+} (1.42 Å) is much larger than that of La^{3+} and having these two cations

randomly distributed would be expected to cause considerable local strain. Ordering of the cations could relieve this strain. As we know that no long range ordering is present we propose that short range layered A-site cation ordering may be present. Short range cation ordering has been observed in other perovskite compounds.¹⁵ For a BM structure with single layers of A-site cations still leaves all the tetrahedral layers with the same environment, so the most reasonable model would involve regions where the ordering is at least 2 layers thick, ensuring that the tetrahedral layers surrounded by only Ba or only La cations.

Thus, we propose a model of short range cation order based on bi-layers, as shown in Figure 2. Bi-layer ordering will relieve the strain caused by the size mismatch between Ba and La by producing two very different inter-octahedral layer distances. This creates another issue which is that tetrahedra of the same size now need to span different inter-octahedral layer distances. This can be accommodated by having different amounts of twisting within the tetrahedral layers. The tetrahedral layers within Ba bi-layers need to span a large distance and so they twist very little or not at all. As their twist angle is small, the tetrahedral chains have negligible dipole moments and so would likely twist in the same direction. The tetrahedral layers within a La bi-layer are compressed due to being between octahedral layers that are about half an angstrom closer together than those within a Ba bi-layer. To accommodate this they twist heavily, producing large dipole moments within the chains which lead to an intra-layer ordering of two different twist directions. It should be noted that since this ordering is not long range there must be frequent deviations from this pattern, such as quadruple layers or a change in the direction of the layered ordering and tetrahedral chains, so that the structure averages to cubic over long distances.

The next question is whether or not such a model is consistent with the PDF data. There is some evidence to suggest there are two distinct inter-layer distances in the structure. There is a peak in the PDF at ~ 8.4 Å that falls at the expected inter-layer distance (Fig. 3). While this is not twice the cubic lattice parameter for this compound, in the closely related BM phase with composition $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_{2.5}$ the layered direction is significantly elongated compared to the in-plane directions. This means that the direction normal to the layering is expected to be longer than twice the average cubic length. As the inter-layer distance is 8.26 Å in $\text{La}_{0.7}\text{Ba}_{0.3}\text{Mn}_2\text{O}_{2.5}$ and since this distance is expected to increase with increasing Ba content, the peak at ~ 8.4 Å can be ascribed to inter-layer distances. This peak shows a clear splitting into two peaks at 8.34 Å and 8.50 Å which could indicate two distinct inter-layer distances in the structure. Since this peak is small the PDF was generated using several different Q_{max} values and it was found to be present regardless, confirming it is a real structural feature and not a termination artifact. The PDFgui refinements were not able to model this splitting with any of the four BM model structures or the $\text{BaLaMn}_2\text{O}_5$ model. Even when all the parameters were allowed to refine these models only produced a single peak in this vicinity.

The fitting results show that the local structure of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ most closely resembles a brownmillerite structure, but with a variety of inter-octahedral layer relationships.

This means that the structure retains the basic structural units of the earlier members of the $\text{La}_{1-x}\text{Ba}_x\text{MnO}_{2.5}$ series, only without long range order, instead of locally resembling the structure of the thermodynamic version of this composition. The structure of $\text{BaLaMn}_2\text{O}_5$ is driven by the need to satisfy the much different coordination preferences of the La and Ba cations. In this structure the vacancies are only found in the La layer, such that La has a coordination number of 8 while the larger Ba has a coordination number of 12. As $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ is prepared at quite low temperatures, cation diffusion is very unlikely. Therefore, the La/Ba segregation in this compound was likely present in the precursor compound $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$. While the local structure of this compound has not been studied there is likely some short range segregation to avoid the large strain of having a truly random distribution. When this compound is reduced a BM structure is preferred since the Ba and La are not arranged in a manner which allows the oxygen vacancies to occur only around La cations as would be the case if it was prepared at a high enough temperature for cation diffusion. In related $\text{La}_{1-x}\text{Ba}_x\text{MnO}_{2.5}$ compounds where the Ba concentration is low it is possible to have a long range ordered BM structure since regular inter-layer relationship can exist, but when the Ba concentration is too high different inter-layer distances are needed to accommodate the A-cation size difference, which prevents any long range order.

3.3 Local Structure of $\text{BaY}_{0.25}\text{Fe}_{0.75}\text{O}_{2.5}$. The average cubic structure of $\text{BaY}_{0.25}\text{Fe}_{0.75}\text{O}_{2.5}$ has a single $B\text{--O}$ bond distance of 2.08 Å. This implies that both Fe--O and Y--O bonds are of the same length. Considering the very different ionic radii of Fe^{3+} (0.55 Å) and Y^{3+} (0.90 Å) it can be expected that the local structure must deviate greatly from the cubic average in order to accommodate this huge size difference. The first peak in the PDF representing the $B\text{--O}$ distances has a more complex shape than would be produced by a single bond distance (Fig. 4). There is a strong, sharp peak at 1.88 Å followed by a broad feature which peaks at 2.17 Å. A bond distance of 1.88 Å is exactly what is expected for Fe^{3+} coordinated by 4 oxygen atoms. The presence of a large amount of 4 coordinate Fe is not surprising considering that basic chemical considerations would suggest that the Y^{3+} would prefer to always have a coordination number of at least 6 and therefore the oxygen vacancies would be expected to be distributed between pairs of Fe atoms. The broad peak at 2.17 Å is close to the expected bond distance for 6 coordinate Y^{3+} to oxygen (2.27 Å) but slightly shorter, which suggests that this broad feature includes the Y--O distances as well as some bonds from 5 or 6 coordinate Fe. Fitting the PDF with the average structure model obviously produces a very poor fit to the low- r region of the PDF as it produces just a single peak at 2.08 Å, which is near the minimum between the two actual peaks in the PDF (Fig. 4). This shows that there are actually very few bond distances near the average bond length. The average structure model provides a much better fit at distances beyond one unit cell, showing that the displacements from the average structure do not correlate very far (Fig. S9). However, the fits with the average structure do not become fully satisfactory unless the refinement is done with a minimum distance of ~30 Å or greater.

A number of different model structures were fit against the PDF in order to gain insight into the local coordination environments present. One structure type to consider would, of

course, be the brownmillerite since, as already noted, this is a common structure type for oxygen deficient perovskites. A number of different BM models were fit using both PDFgui and RMCProfile. These models had octahedral layers which were half occupied by Y and half occupied by Fe alternating with tetrahedral layers which were pure Fe. None of these models could not provide a good fit to the low- r region of the PDF. The primary issue was an under-fitting of the first sharp peak at 1.88 Å and an over-fitting of the second peak at 2.17 Å. This implies that there is probably only a small level of octahedral Fe and most Fe is 4 coordinate with some 5 coordination Fe as well. It is perhaps not surprising that the BM models were unable to produce good fits since in this structure the octahedral and tetrahedral layers must be the same size. Having all the Y in one layer puts considerable strain on the system and prevents the ions from obtaining their ideal coordination environments.

Other models were considered which would be able to relieve the bond strain caused by the large size of the Y. The most disordered of these models will be discussed first. Typically in perovskites with two B -site cations of very different size rock-salt ordering is observed as this is the most effective way to accommodate the size difference. However, rock-salt ordering occurs for a 1:1 cation ratio while $\text{BaY}_{0.25}\text{Fe}_{0.75}\text{O}_{2.5}$ has a 3:1 ratio. A “semi-rock-salt” model was created in which there are two distinct B -sites which are rock-salt ordered. One of these sites is always occupied by Fe and the other is randomly occupied by Fe half the time and Y half the time. The oxygen vacancies were distributed such that they never occur next to a Y but are randomly distributed among the anion sites that occur between two Fe cations. This model has a large degree of local order but does not lead to any long range order. It also has the advantage that the Y are always octahedrally coordinated, the Fe have an average coordination of 4.67, and the Y never neighbor other Y and are distributed equally in all directions as so not to create strain. This model was created in an RMC supercell by swapping atoms with appropriate constraints before allowing the atoms to move in the regular refinement. The refinement using this model was superior to the BM model at all length scales. The fit above ~ 4 Å was very good and the best of all the models tested. This shows that this model is a good approximation of what the structure looks like at medium length scales. Fitting of the low- r region was still problematic, with the most significant issue being that there was still an under-fitting of the first peak at 1.88 Å and an over-fitting of the second peak at 2.17 Å.

Another model to consider is one based on the structure of the closely related compound $\text{Ba}_4\text{CaFe}_3\text{O}_{9.5}$.¹⁶ This structure has a complex pattern of cation and anion ordering based on stacking of CaFe_3O_7 layers which are separated, alternately, by Ba_4O_2 and Ba_4O_3 layers. In $\text{Ba}_4\text{CaFe}_3\text{O}_{9.5}$ the shifts of the CaFe_3O_7 layers relative to the neighboring layers are fully determined by the need to prevent CaO_6 units from neighboring each other and to minimize the bond strains in the structure. If additional oxygen is added to the system such as would be the case for $\text{BaY}_{0.25}\text{Fe}_{0.75}\text{O}_{2.5}$ ($\text{Ba}_4\text{YFe}_3\text{O}_{10}$), only Ba_4O_3 layers would exist. In this case there become two possibilities for the relationships between CaFe_3O_7 layers. Such a situation would preserve the local order while not requiring long range order. Such a model was constructed as an RMC supercell by taking the $\text{Ba}_4\text{CaFe}_3\text{O}_{9.5}$ structure, replacing Ca with Y, adding additional

oxygen, and creating both types of allowed inter-layer relationships (Fig. S10). This model provided a slightly better fit to the low- r region of the PDF, although the first peak was still slightly under-fit.

A final possibility to consider is that the local structure of $\text{Ba}_4\text{YFe}_3\text{O}_{10}$ is related to other structures within the $\text{Ba}_n\text{YFe}_{n-1}\text{O}_{2.5n}$ series.^{9,17} The $n=2$ and $n=3$ members of this series have complex structures which have been well characterized. The structure of the $n=3$ compound has a feature which appears consistent with the PDF. $\text{Ba}_3\text{YFe}_2\text{O}_{7.5}$ consists of $\text{Y}_2\text{Fe}_2\text{O}_{10}$ slabs which are connected by dimers of FeO_4 tetrahedra. An important aspect of these dimers not specifically pointed out in earlier work is that each FeO_4 tetrahedron in a dimer has a terminal oxygen atom which is not connected to another Fe or Y atom. These terminal O atoms instead make an unusually short bond to a Ba atom. The result of having terminal oxygen atoms is that the coordination number of the Fe atoms are lower than would be expected for a perovskite with this oxygen content. In $\text{Ba}_3\text{YFe}_2\text{O}_{7.5}$ we would expect 1/2 of the Fe atoms to have a coordination numbers of 5 while 1/2 have a coordination number of 4, assuming Y always has a coordination number of 6 and the corner sharing connectivity is maintained. However, because the connectivity is broken all Fe in $\text{Ba}_3\text{YFe}_2\text{O}_{7.5}$ have a tetrahedral coordination environment. Having more tetrahedral Fe than expected based on the composition is consistent with the difficulty the other structural models have had in fitting the strong peak at 1.88 Å. The local structure of $\text{BaY}_{0.25}\text{Fe}_{0.75}\text{O}_{2.5}$ cannot be the same as the crystal structure of $\text{Ba}_3\text{YFe}_2\text{O}_{7.5}$ due to the different stoichiometry and the fact that Fe cannot simply be put on a Y site. Therefore, a new structural model was developed which accommodates the cation ratios but allows for the presence FeO_4 dimers with terminal O atoms. This model used the $\text{Ba}_3\text{YFe}_2\text{O}_{7.5}$ structure as a starting point. Instead of having two dimensional slabs of $\text{Y}_2\text{Fe}_2\text{O}_{10}$, there are single columns of alternating FeO_4 and YO_6 . These columns are connected by Fe dimeric units. However, since there are now fewer Y atoms one of the Fe in each dimer now has a coordination number of 5 instead of 4 and some terminal O positions are used to connect the columns. This new structural model is shown in Figure 5. While this structure does not have all Fe in tetrahedral coordination the average coordination number of the Fe is reduced. In this model 2/3 of the Fe are tetrahedral and 1/3 are square pyramidal, while the other models have 1/3 tetrahedral and 2/3 square pyramidal. This new structural model was converted into an RMC supercell and used for refinement (Fig. 6). This model provides the best fit of any of the models to the low- r region of the PDF, although it is not significantly better than the fit with the $\text{Ba}_4\text{CaFe}_3\text{O}_{9.5}$ derived model.

The fitting results seem to show that in the local structure there are not neighboring Y atoms, that the oxygen vacancies only occur between Fe atoms, and that there is a greater concentration of short Fe–O bonds than expected. It seems that $\text{Ba}_4\text{YFe}_3\text{O}_{10}$ is best considered a member of the $\text{Ba}_n\text{YFe}_{n-1}\text{O}_{2.5n}$ series and locally retains some of the structural features of $\text{Ba}_3\text{YFe}_2\text{O}_{7.5}$, most notably the presence of terminal O atoms giving rise to more tetrahedral Fe than expected for a perovskite of this composition. However, the fit using a $\text{Ba}_4\text{CaFe}_3\text{O}_{9.5}$ structure with extra oxygen gives an almost as good fit and cannot be excluded as a possibility. It could also be that structural units related to both of these structure types exist locally.

4. Conclusions

Neutron pair distribution function data clearly show that there is a large degree of short range cation and anion vacancy ordering in the oxygen deficient perovskites $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ and $\text{BaY}_{0.25}\text{Fe}_{0.75}\text{O}_{2.5}$, leading to local structures which are quite different from the average cubic structures of these compounds. $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ is shown to have a brownmillerite type of short range order in the sense that there are alternating layers of MnO_6 octahedra and MnO_4 tetrahedra. This makes it similar to other members of the $\text{La}_{1-x}\text{Ba}_x\text{MnO}_{2.5}$ series with smaller x values which have brownmillerite crystal structures. However, in $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ there appears to be a variety of inter-layer relationships such that $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ cannot be described as locally being like any single brownmillerite variant. We propose that short range ordering of the much differently sized La and Ba cations creates layers of different thicknesses, which in turn promotes different patterns of twisting within and between the tetrahedral layers. This local variation is likely why this series loses long range order at lower x values than in the related Ca and Sr series. On the other hand, $\text{BaY}_{0.25}\text{Fe}_{0.75}\text{O}_{2.5}$ does not have a local brownmillerite structure but instead seems to be structurally similar to other $\text{Ba}_n\text{YFe}_{n-1}\text{O}_{2.5n}$ compounds. In particular, it seems to have more tetrahedral Fe than was expected, which is attributed to the presence of some terminal oxygen atoms in Fe centered dimers. In this sense it has similar building blocks to $\text{Ba}_3\text{YFe}_2\text{O}_{7.5}$ but with lower dimensionality, which is probably related to the lack of long range order. These results increase our understanding of how synthesis conditions, cation order, and anion order are inter-related, which can help to guide the design of ionic conducting materials. This study also highlights how local structures can sometimes be more complex than being simple analogs to a single known crystal structure.

Acknowledgements

This work has benefited from the use of NPDF at the Lujan Center at Los Alamos Neutron Science Center, funded by DOE Office of Basic Energy Sciences. Los Alamos National Laboratory is operated by Los Alamos National Security LLC under DOE Contract DE-AC52-06NA25396.

Site	Occupancy	Coordinates (x,y,z)	U _{iso} (Å ²)
La _{0.5} Ba _{0.5} MnO _{2.5}			
La/Ba	0.5/0.5	½, ½, ½	0.0439(6)
Mn	1	0, 0, 0	0.0172(4)
O	0.833	½, 0, 0	0.0956(6)
BaY _{0.25} Fe _{0.75} O _{2.5}			
Ba	1	½, ½, ½	0.0298(6)
Y/Fe	0.25/0.75	0, 0, 0	0.0533(6)
O	0.833	½, 0, 0	0.0565(6)

Table 1. Results of Rietveld refinements in space group *Pm-3m* (#221). For La_{0.5}Ba_{0.5}MnO_{2.5} the lattice parameter refined to $a = 4.0092(1)$ with $\chi^2 = 21.75$, while BaY_{0.25}Fe_{0.75}O_{2.5} has $a = 4.1592(1)$ with $\chi^2 = 18.39$.

Fit Range (Å)	R _w	La/Ba U _{iso}	Mn U _{iso}	O U _{iso}
1.5-5.5	27.9	0.030	0.003	0.062
5-15	21.0	0.024	0.012	0.086
15-30	13.0	0.018	0.023	0.077

Table 2. Parameters from selected fits of the PDF of La_{0.5}Ba_{0.5}MnO_{2.5} using the average structure as a model.

Space group	R_w for 1.5-5.5 Å	R_w for 6-12 Å	R_w for 1.5-20 Å	R_w for 12-30 Å
<i>I2mb</i>	6.8	10.5	17.0	9.6
<i>Pnma</i>	5.1	8.0	15.6	10.3
<i>Pcmb</i>	6.4	5.0	13.2	17.7
<i>C2/c</i>	6.2	5.3	12.7	8.4

Table 3. Fitting parameters for fits to the PDF of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ done over various r -ranges with different structural models.

Figure 1. The low- r region of the PDF of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ and the fit using the average cubic structure as a model.

Figure 2. A representation of the local structure of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$. The small blue spheres are Mn, the small red spheres are O, the large gray spheres are La, and the large orange spheres are Ba. The alternating octahedral and tetrahedral layers of the brownmillerite structure are shown as is the proposed short range segregation of the La and Ba cations. This figure was created with *Pcmb* style twisting of the tetrahedral chains, although in reality it is suspected that a variety of twisting patterns are present. The PDF data suggest that the inter-layer spacing in the Ba rich regions is greater than in the La rich regions.

Figure 3. The PDF of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ showing the splitting of the peak centered around 8.4 Å, revealing that there are different inter-layer distances in this compound.

Figure 4. The low- r region of the PDF of $\text{BaY}_{0.25}\text{Fe}_{0.75}\text{O}_{2.5}$ and the fit using the average cubic structure as a model.

Figure 5. The model constructed as the starting point for RMC refinements of BaY_{0.25}Fe_{0.75}O_{2.5} with terminal oxygen atoms. The large gray atoms are Ba, the large purple atoms are Y, and the small green atoms are Fe. The O atoms are labeled red, except for the terminal O atoms which are orange.

Figure 6. A comparison of the RMC fits of different models to the low- r region of the PDF of $\text{BaY}_{0.25}\text{Fe}_{0.75}\text{O}_{2.5}$.

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