Supporting Information for:

Identifying the Local Structural Units in $La_{0.5}Ba_{0.5}MnO_{2.5}$ and $BaY_{0.25}Fe_{0.75}O_{2.5}$ through the Neutron Pair Distribution Function

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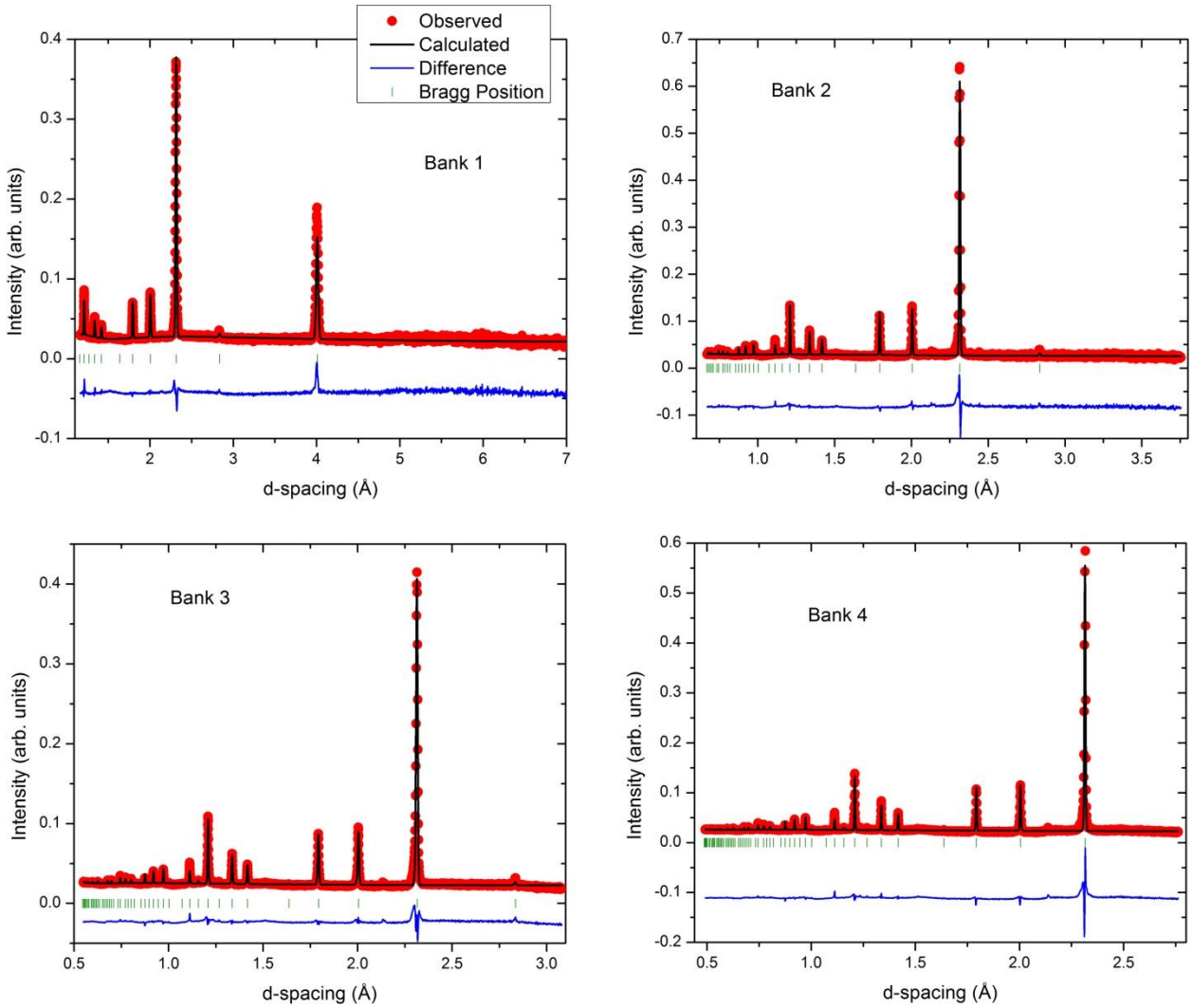

Figure S1. Rietveld refinement of the powder neutron diffraction pattern of $La_{0.5}Ba_{0.5}MnO_{2.5}$.

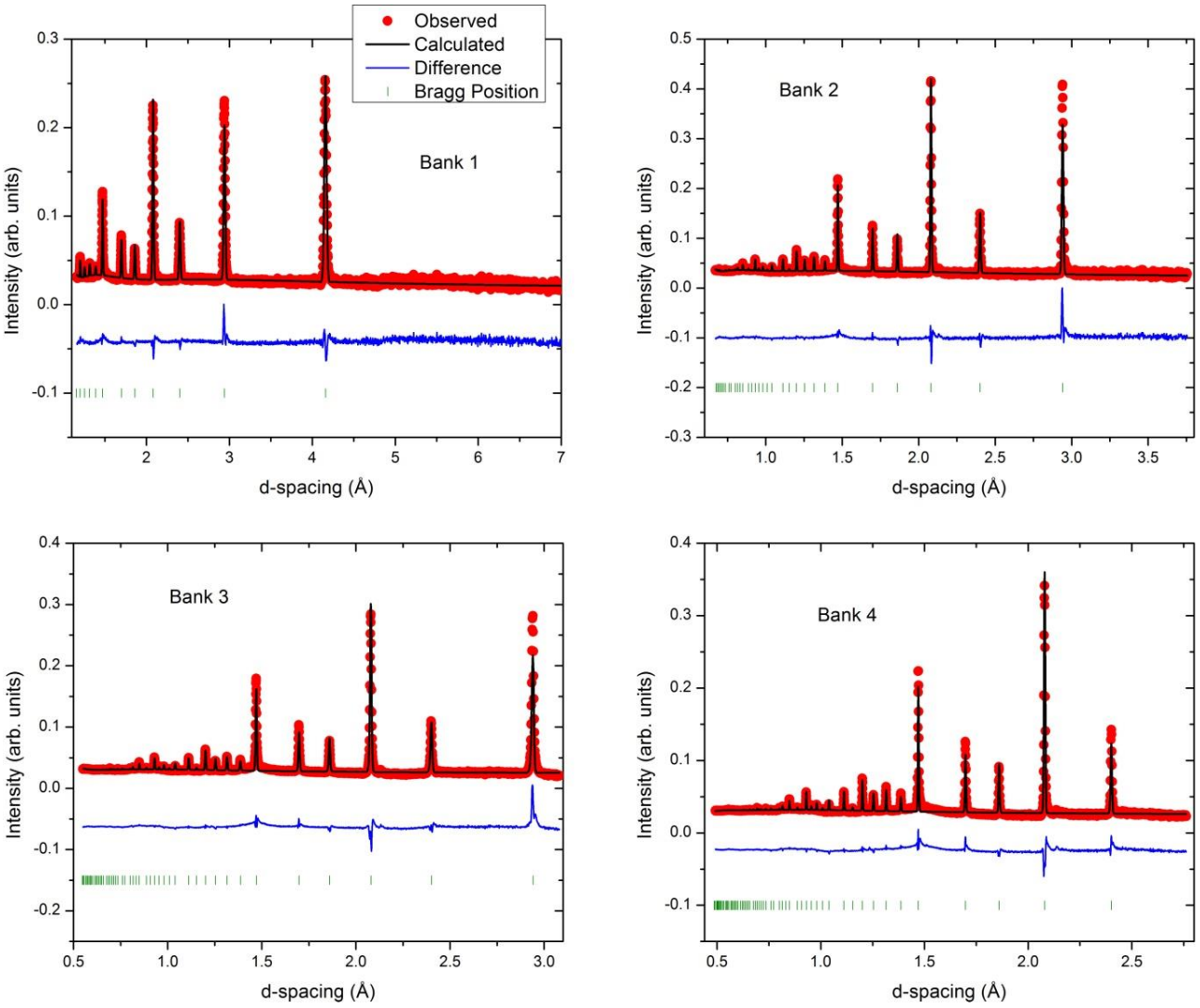

Figure S2. Rietveld refinement of the powder neutron diffraction pattern of $BaY_{0.25}Fe_{0.75}O_{2.5}$.

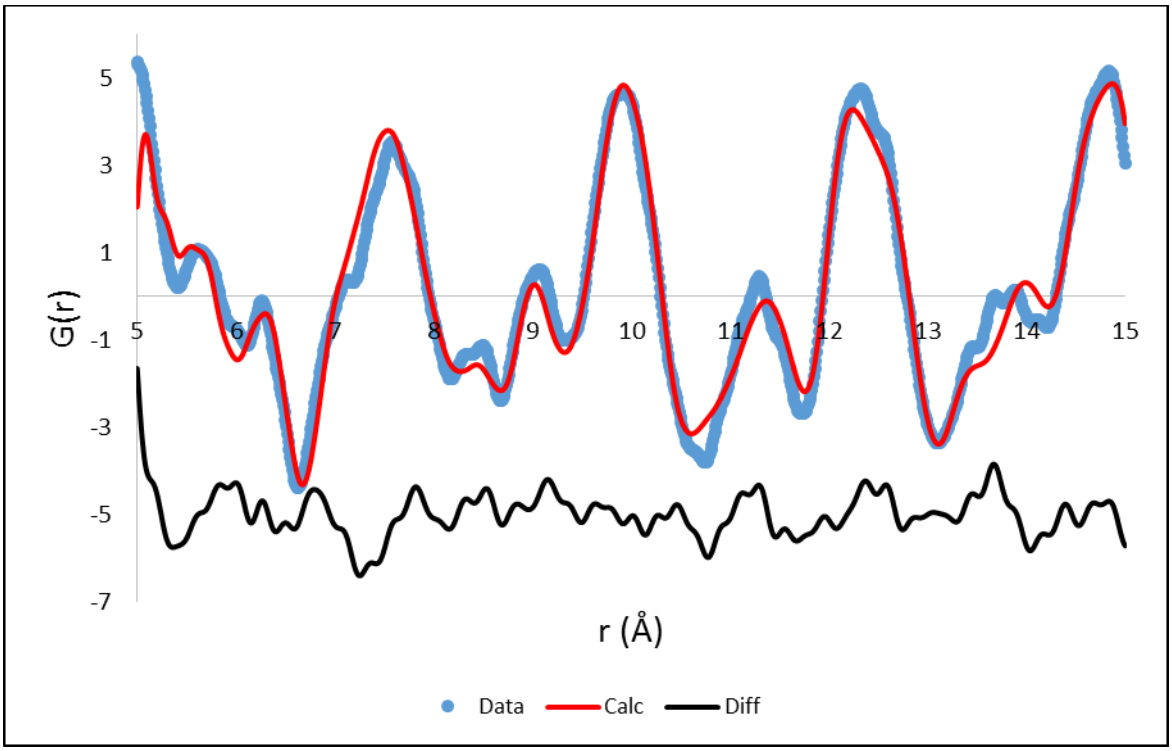

Figure S3. The fit to PDF of $La_{0.5}Ba_{0.5}MnO_{2.5}$ using the average structure as a model over an *r*-range of 5-15 Å, showing how the fit at medium-*r* is better than at low-*r* but still has significant issues.

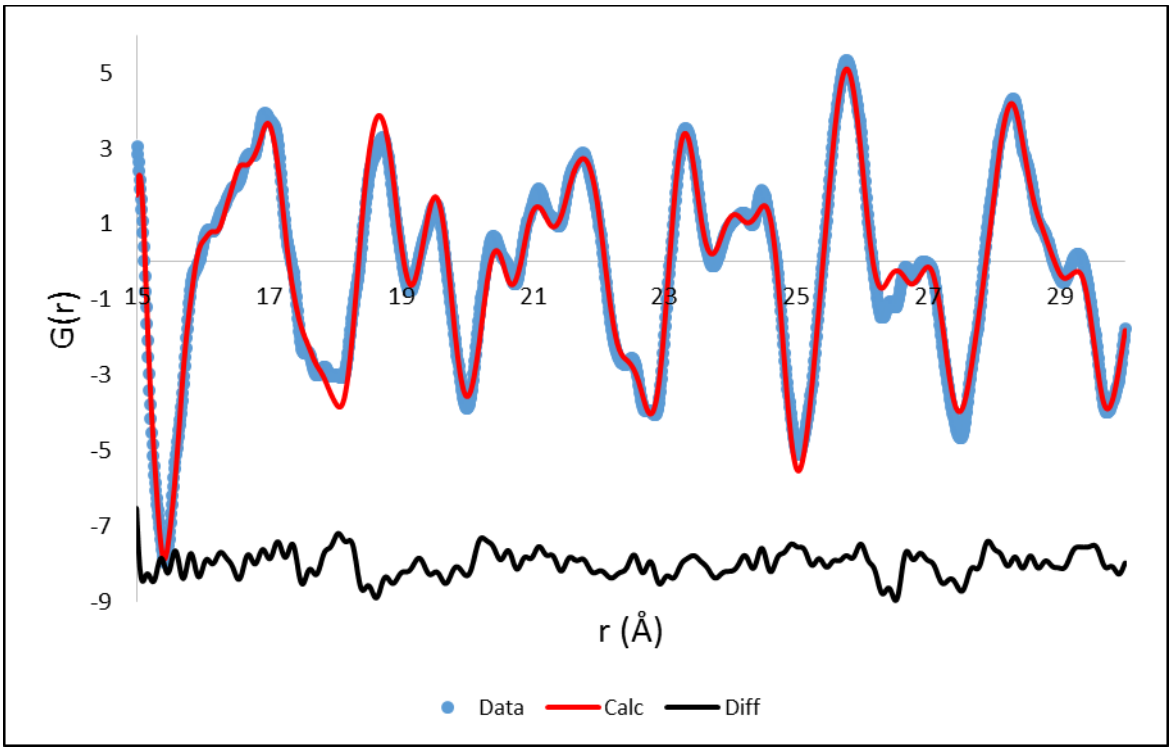

Figure S4. The fit to PDF of $La_{0.5}Ba_{0.5}MnO_{2.5}$ using the average structure as a model over an *r*-range of 15-30 Å, showing how at longer length scales the fit becomes almost satisfactory.

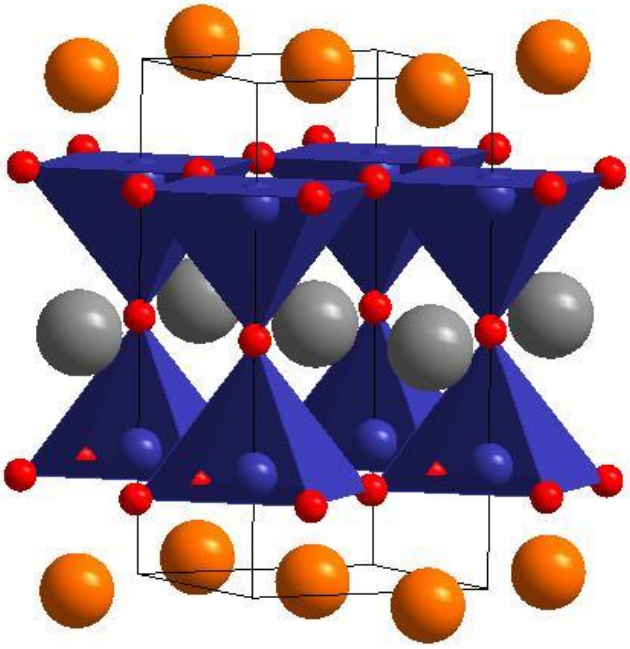

Figure S5. The crystal structure of the cation and anion vacancy ordered compound $LaBaMn_2O_5$. Blue atoms are Mn, red atoms are O, gray atoms are Ba, and orange atoms are La.

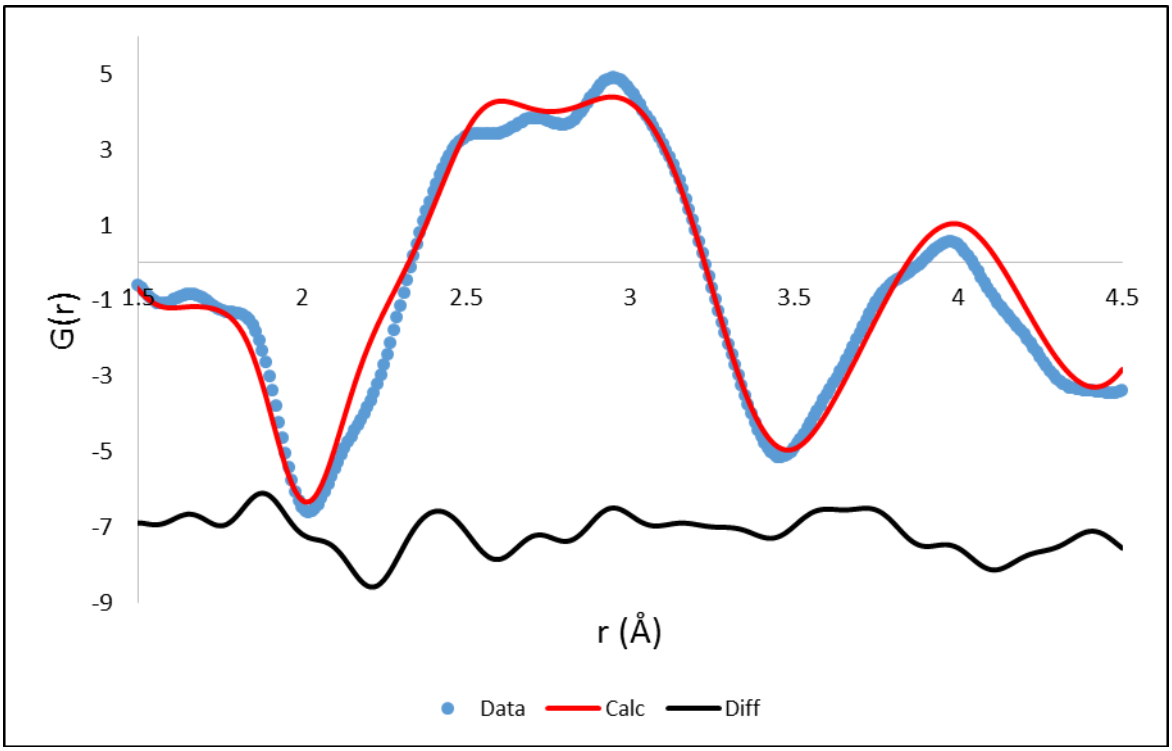

Figure S6. The fit to the low-*r* region of the PDF of $La_{0.5}Ba_{0.5}MnO_{2.5}$ using the crystal structure of $LaBaMn_2O_5$ as a model. Notice how the first peak corresponding to Mn-O distances cannot be fit with this model, indicating that the coordination of the Mn is not exclusively or almost always square pyramidal. The fit to the higher-*r* peaks is also somewhat poor.

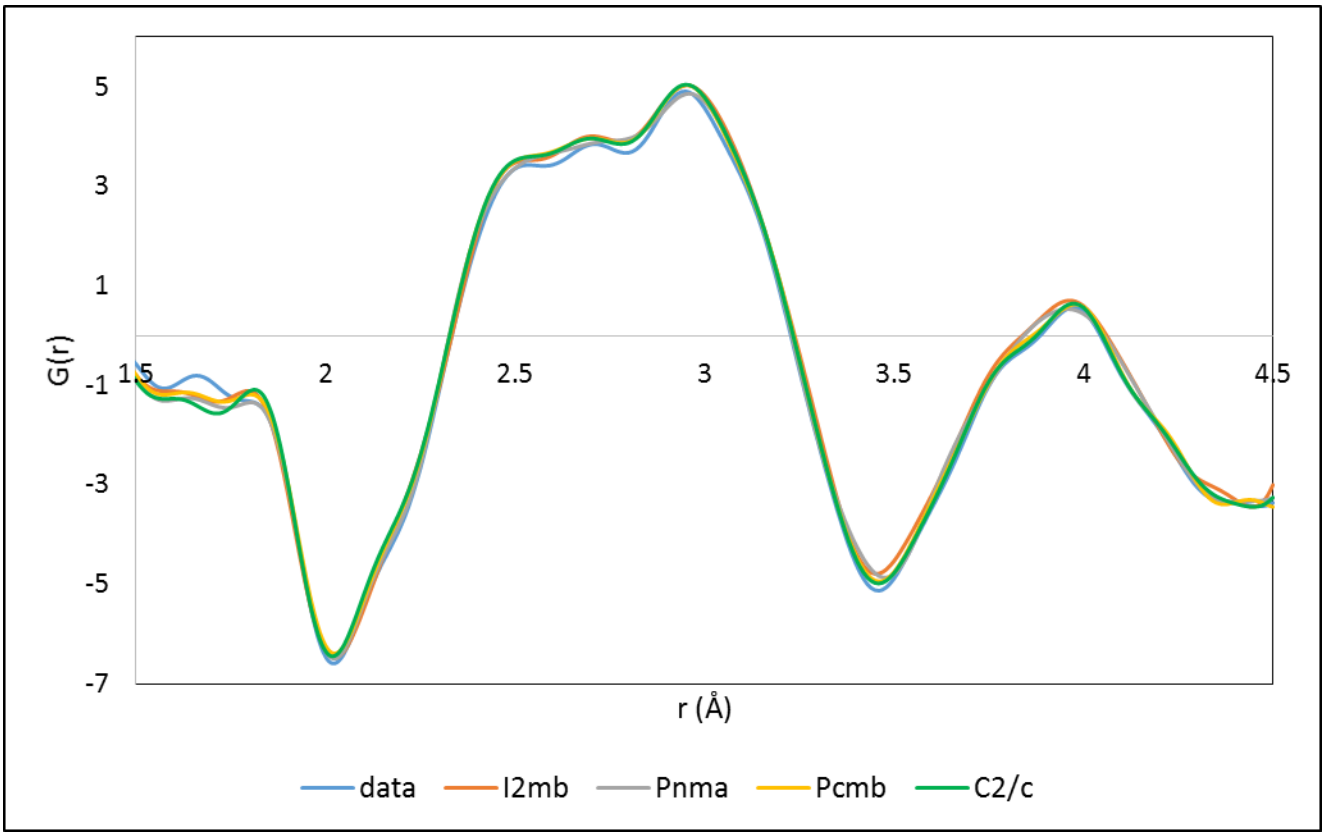

Figure S7. The fit to the PDF of $La_{0.5}Ba_{0.5}MnO_{2.5}$ using four brownmillerite models with different space group symmetries. The strong overlap of all plots shows that any brownmillerite model can fit the low-*r* data since the differences between the models do not become significant until larger *r*-spacing when inter-tetrahedral-chain distances appear.

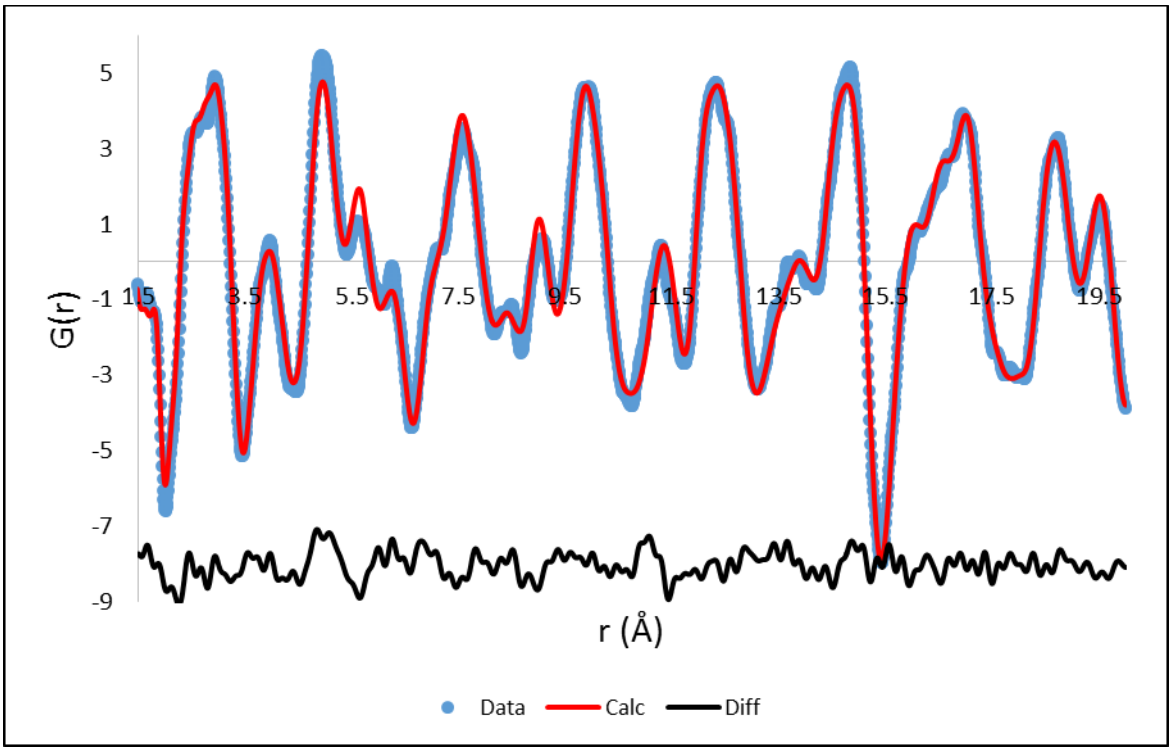

Figure S8. The fit to the PDF of $La_{0.5}Ba_{0.5}MnO_{2.5}$ from 1.5 to 20 Å using a *C*2/*c* model. The fit is almost sufficient but still has significant deficiencies. Notice how the worst fit region is around distances corresponding to the first inter-layer spacing. The fits using the other brownmillerite models are similar but slightly worse.

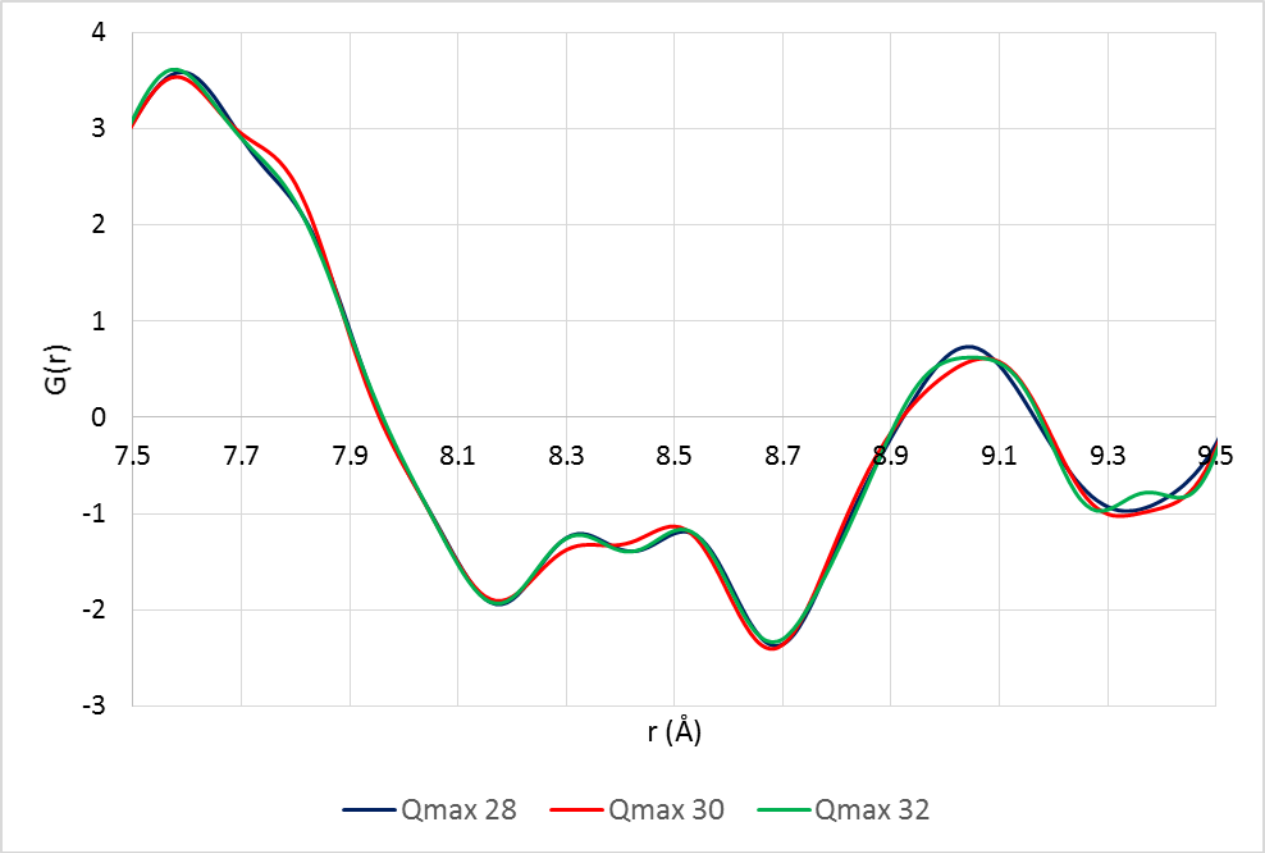

Figure S9. The PDF of $La_{0.5}Ba_{0.5}MnO_{2.5}$ generated using three different Q_{max} values for the S(Q). This demonstrates that the splitting of the small peak at ~8.4 Å is present regardless of the Q_{max} value and is therefore due to structural effects and not termination noise.

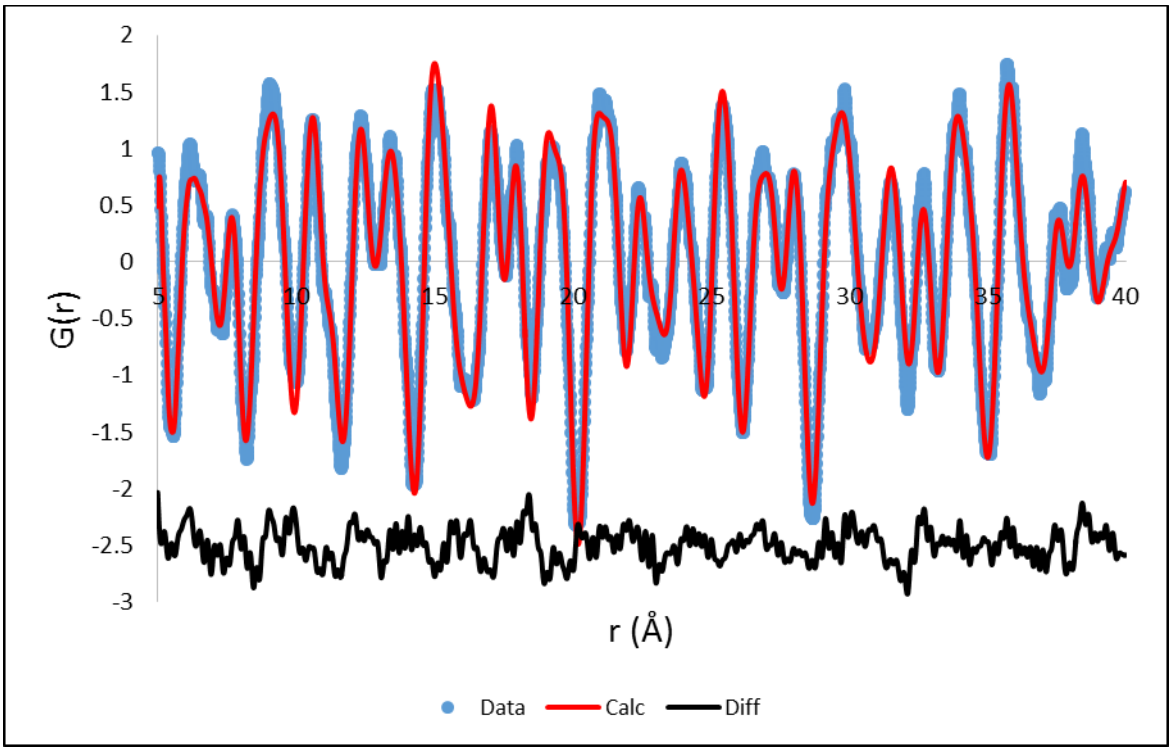

Figure S10. The fit to the PDF of $BaY_{0.25}Fe_{0.75}O_{2.5}$ using the average cubic structure as a model over an *r*-range of 5-40 Å.

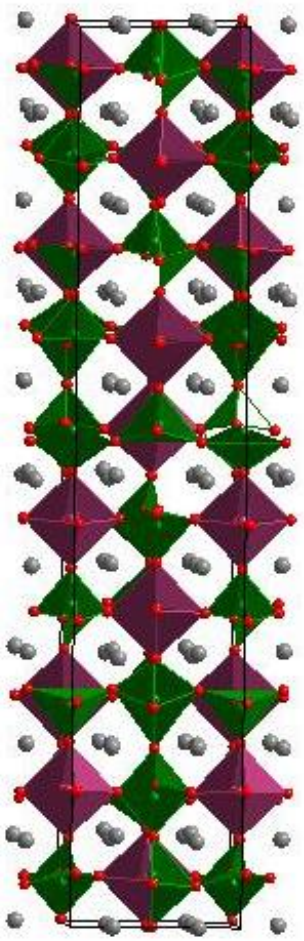

Figure S11. The model structure for $BaY_{0.25}Fe_{0.75}O_{2.5}$ based on a modified $Ba_4CaFe_3O_{9.5}$ structure. This model structure has lattice parameters of a = 8.19 Å, b = 8.17 Å, and c = 43.07 Å and all angles 90°. The actual $Ba_4CaFe_3O_{9.5}$ structure is based on an A-B'-D'-C-B-A'-C'-D stacking sequence and has a c lattice parameter of 32.31 Å. In this model there are two possible stacking patterns since both A-B'-D' and A-B'-A are allowed, owing to the higher oxygen content of $BaY_{0.25}Fe_{0.75}O_{2.5}$ ($Ba_4YFe_3O_{10}$) compared to $Ba_4CaFe_3O_{9.5}$. This model has an extra defect stacking sequence added on to it, giving it an A-B'-A-B'-D'-C-B-A'-C'-D pattern. See reference 16 for an explanation of the stacking sequence nomenclature.