

Supporting Information for:

**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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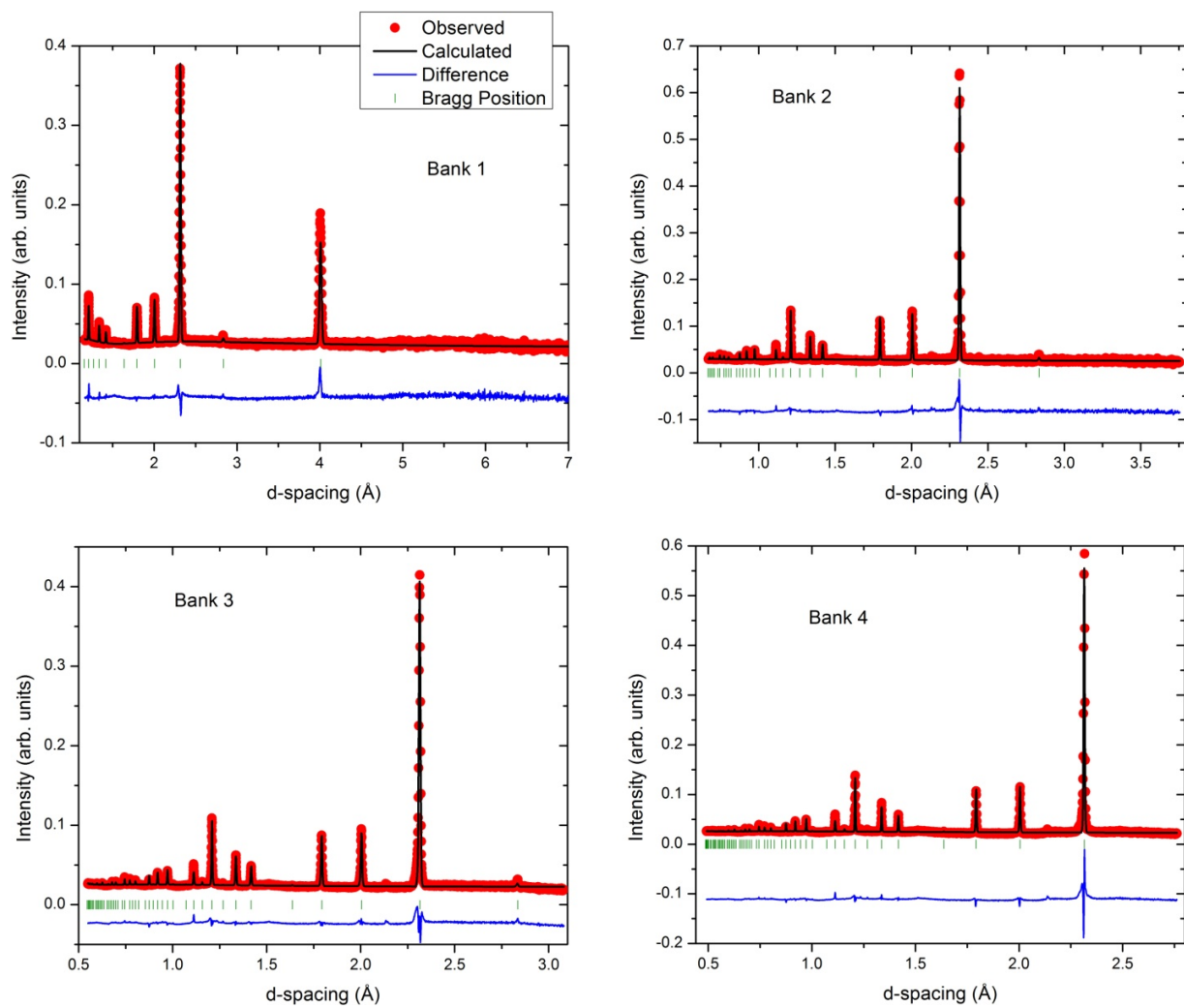


Figure S1. Rietveld refinement of the powder neutron diffraction pattern of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$.

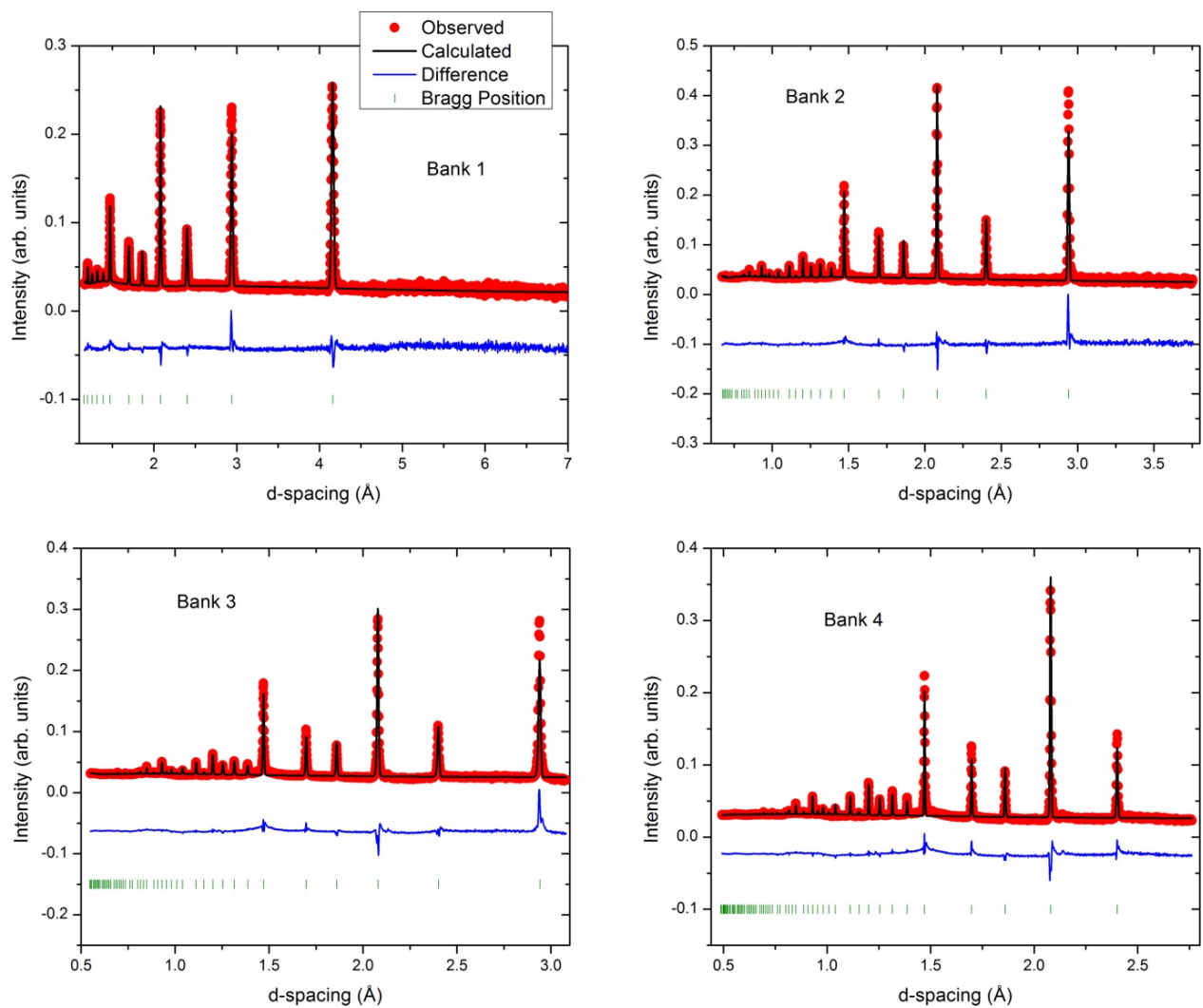


Figure S2. Rietveld refinement of the powder neutron diffraction pattern of $\text{BaY}_{0.25}\text{Fe}_{0.75}\text{O}_{2.5}$.

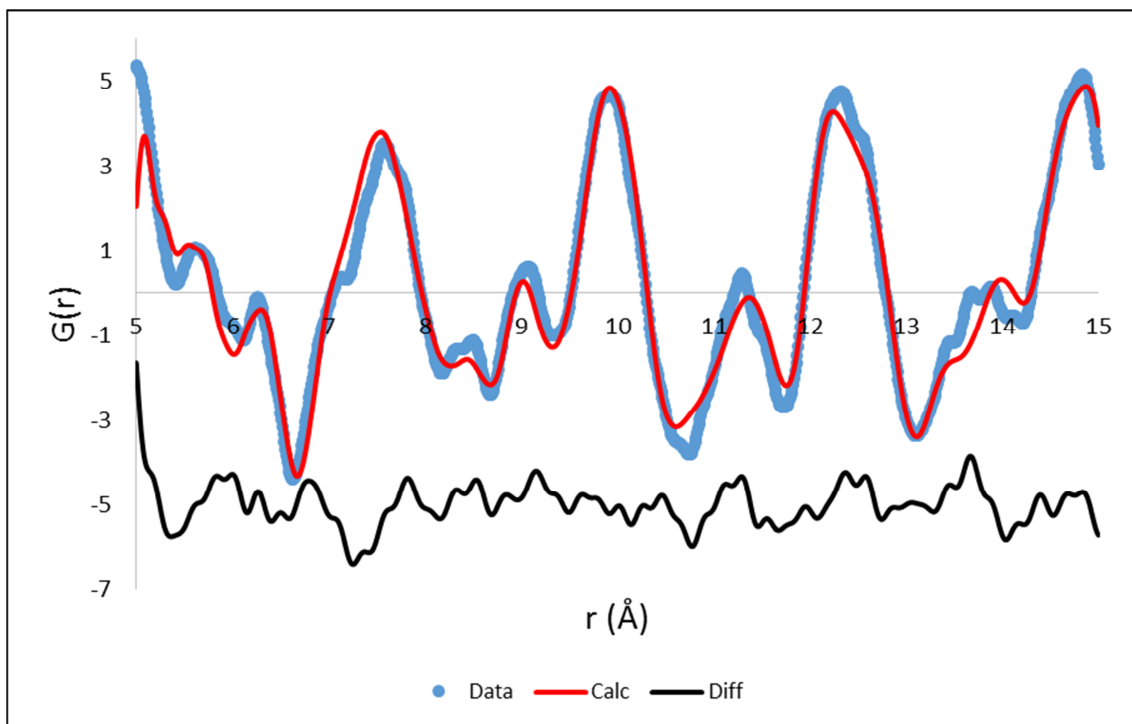


Figure S3. The fit to PDF of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ using the average structure as a model over an r -range of 5-15 Å, showing how the fit at medium- r is better than at low- r but still has significant issues.

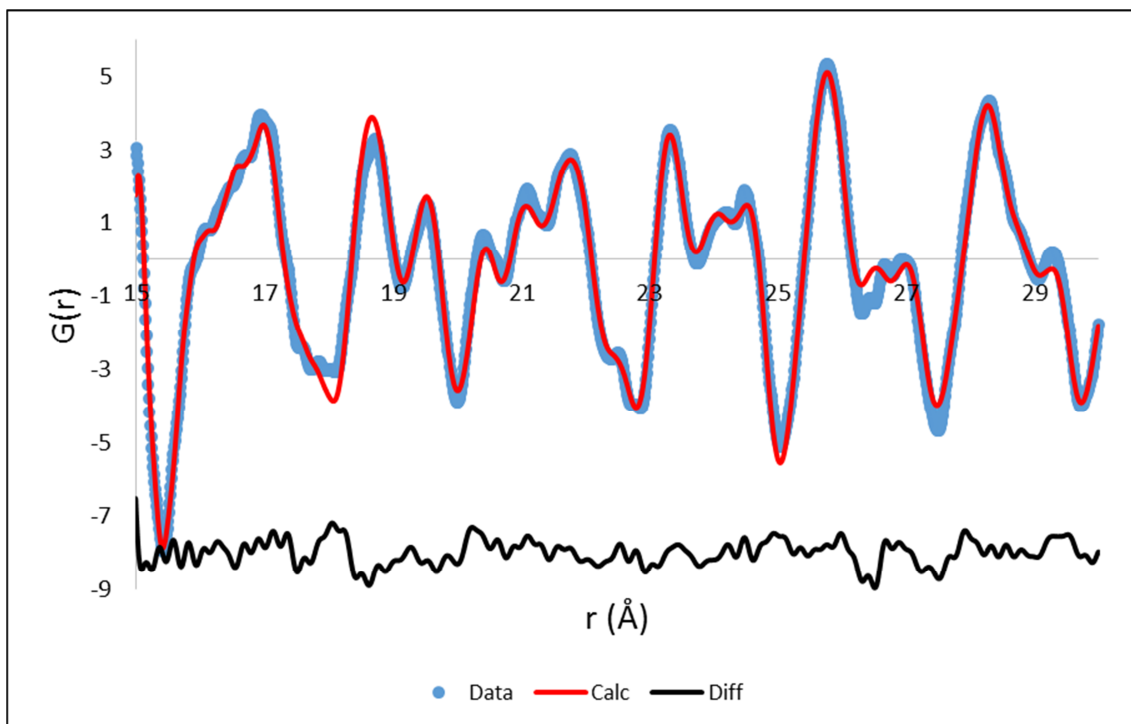


Figure S4. The fit to PDF of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ using the average structure as a model over an r -range of 15-30 \AA , showing how at longer length scales the fit becomes almost satisfactory.

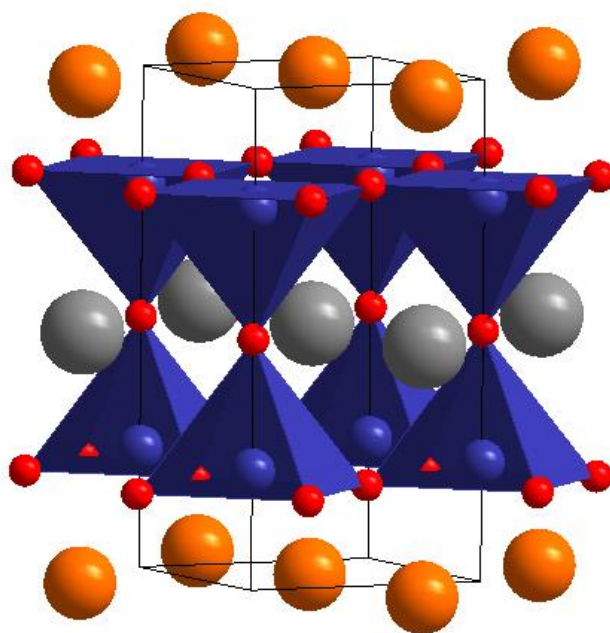


Figure S5. The crystal structure of the cation and anion vacancy ordered compound $\text{LaBaMn}_2\text{O}_5$. Blue atoms are Mn, red atoms are O, gray atoms are Ba, and orange atoms are La.

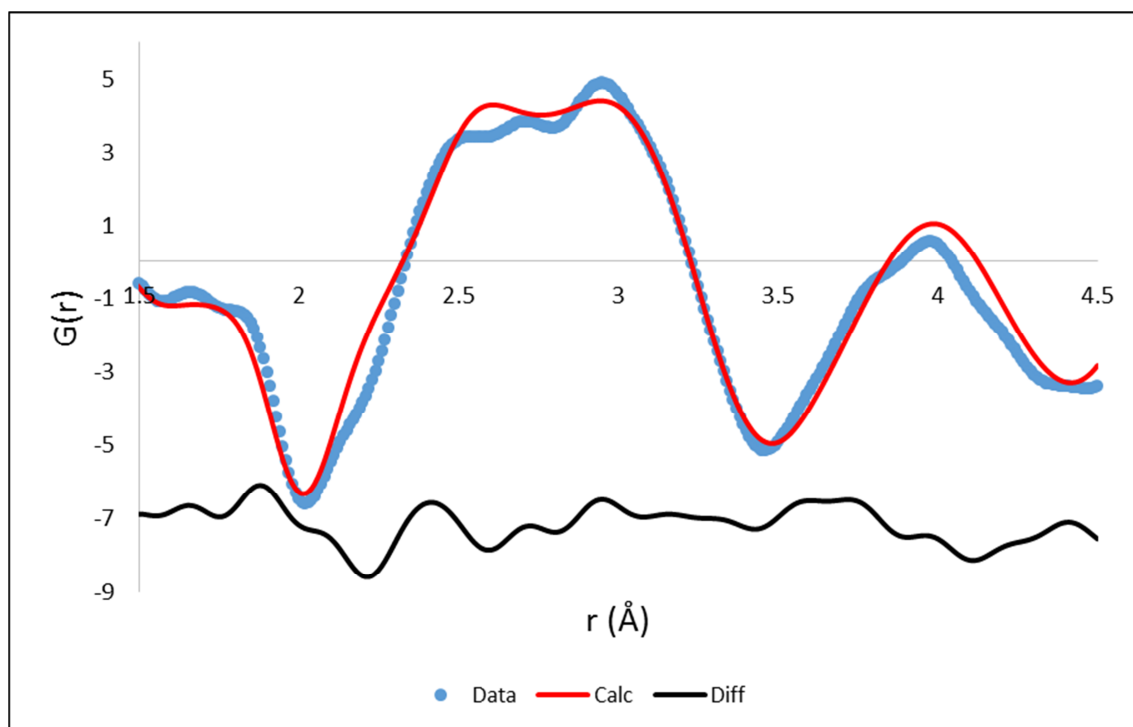


Figure S6. The fit to the low- r region of the PDF of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ using the crystal structure of $\text{LaBaMn}_2\text{O}_5$ as a model. Notice how the first peak corresponding to Mn-O distances cannot be fit with this model, indicating that the coordination of the Mn is not exclusively or almost always square pyramidal. The fit to higher- r peaks is also somewhat poor.

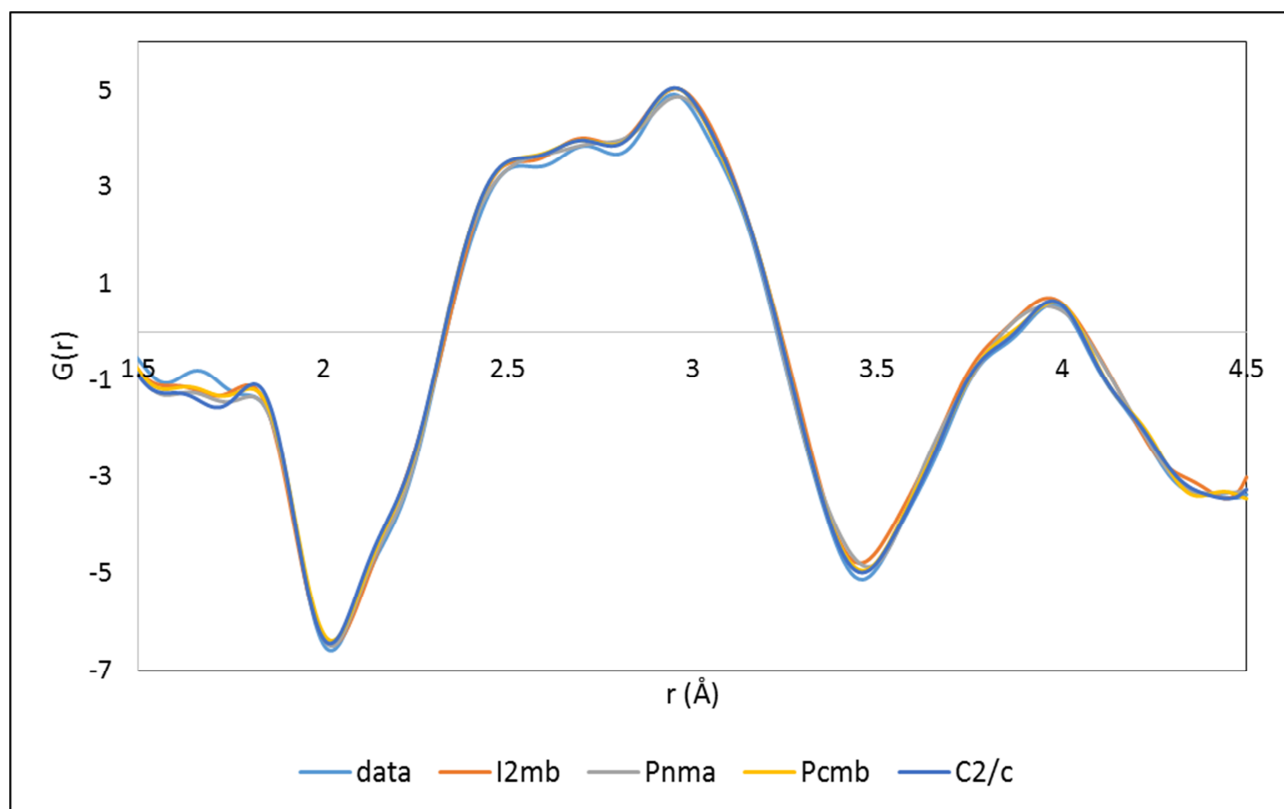


Figure S7. The fit to the PDF of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ using four brownmillerite models with different space group symmetries. The strong overlap of all plots shows that any brownmillerite model can fit the low- r data since the differences between the models do not become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

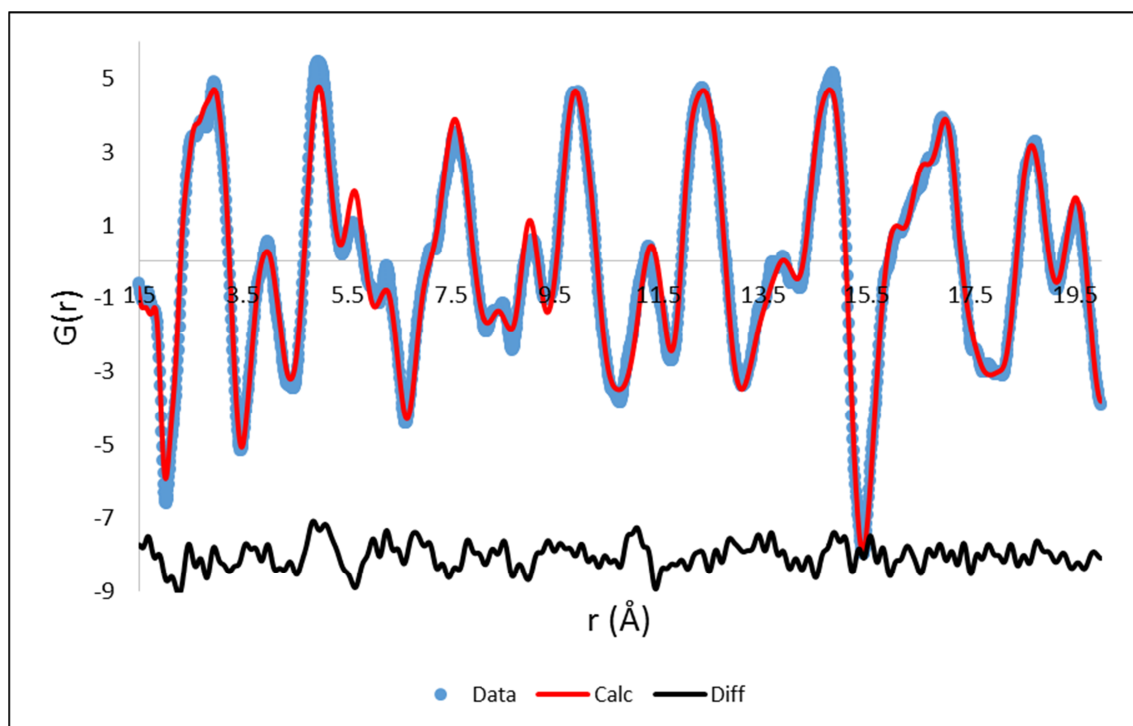


Figure S8. The fit to the PDF of $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{2.5}$ from 1.5 to 20 Å using a $C2/c$ model. The fit is almost sufficient but still has significant deficiencies. Notice how the worst fit region is around distances corresponding to the first inter-layer spacing. The fits using the other brownmillerite models are similar but slightly worse.

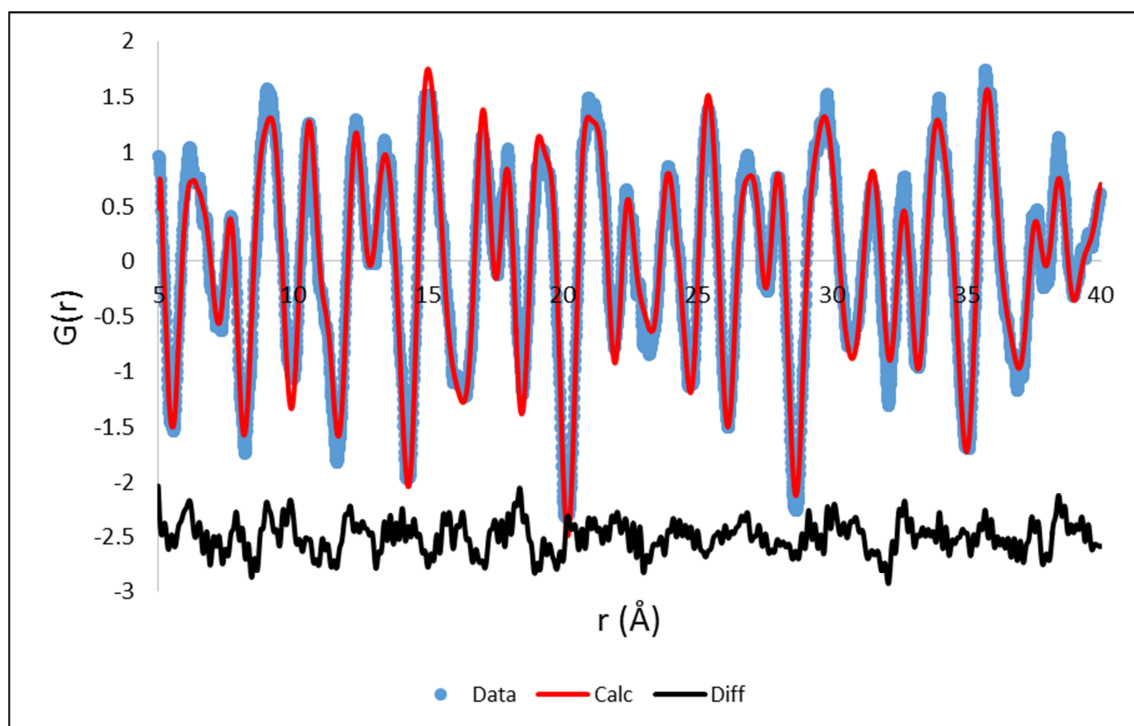


Figure S9. The fit to the PDF of $\text{BaY}_{0.25}\text{Fe}_{0.75}\text{O}_{2.5}$ using the average cubic structure as a model over an r -range of 5-40 \AA .

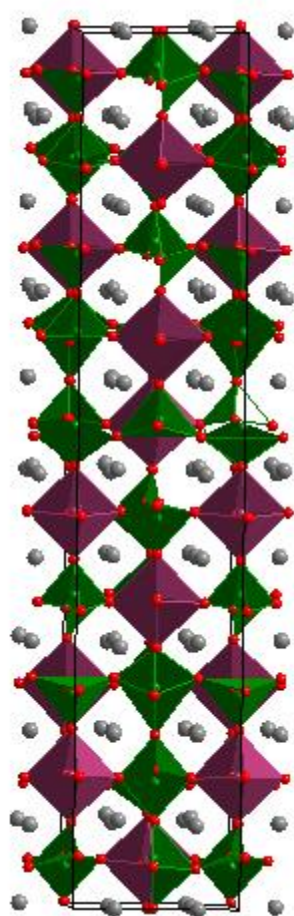


Figure S10. The model structure for $\text{BaY}_{0.25}\text{Fe}_{0.75}\text{O}_{2.5}$ based on a modified $\text{Ba}_4\text{CaFe}_3\text{O}_{9.5}$ structure. This model structure has lattice parameters of $a = 8.19$, $b = 8.17$, and $c = 43.07$ and all angles 90° . The actual $\text{Ba}_4\text{CaFe}_3\text{O}_{9.5}$ structure is based on an A-B'-D'-C-B-A'-C'-D stacking sequence and has a c lattice parameter of 32.31 \AA . 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 $\text{BaY}_{0.25}\text{Fe}_{0.75}\text{O}_{2.5}$ ($\text{Ba}_4\text{YFe}_3\text{O}_{10}$) compared to $\text{Ba}_4\text{CaFe}_3\text{O}_{9.5}$. 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.