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Supporting information: Compositional Influence of Local and Long-Range Polarity in the Frustrated Pyrochlore System $Bi_{2-x}RE_xTi_2O_7$ (RE = Y^{3+}, Ho^{3+})

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All samples were heated at 600 °C to prevent volatilization of bismuth, then heated for 72 hours to final temperatures between 1050-1200 °C as follows. $Bi_{1.5}Y_{0.5}Ti_2O_7$: 9hr at 800 °C, 12hr at 1000 °C, 1050°C, 1100 °C, 1150 °C; $BiYTi_2O_7$: 6hr at 800 °C, 12hr at 1000 °C, 1050 °C, 1100 °C; $Y_2Ti_2O_7$: 12hr at 1000 °C, 12hr at 1100 °C; $Bi_{1.5}Ho_{0.5}Ti_2O_7$: 6hr at 800 °C, 12hr at 1000 °C, 1050 °C; $Bi_{0.5}Ho_{1.5}Ti_2O_7$: 6hr at 800 °C, 12hr at 1150 °C; $Ho_2Ti_2O_7$: 6hr at 800 °C, 12hr at 1150 °C, 1200 °C, 1200 °C.

Table 1: Refined crystallographic data at 300 K for the series $Bi_{2-x}RE_xTi_2O_7$ (RE^{3+}= Y, Ho) with the A-site cation in the ideal 16d position.

Formula	$Bi_{1.52(1)}Y_{0.48(1)}Ti_2O_7$	$Bi_{0.98(2)}Y_{1.02(2)}Ti_2O_7$	$Bi_{0.41(3)}Y_{1.59(3)}Ti_2O_7$	$Y_2Ti_2O_7$
Source	neutron synchrotron	neutron synchrotron	synchrotron	neutron synchrotron
Temperature (K)	300	300	300	300
Space Group	$Fd\bar{3}m$ (#227)	$Fd\bar{3}m$ (#227)	$Fd\bar{3}m$ (#227)	$Fd\bar{3}m$ (#227)
a (Å)	10.27890(6)	10.2200(5)	10.1505(2)	10.0982(2)
Volume a (Å^3)	1086.028(4)	1067.45(20)	1045.85(10)	1029.747(5)
Z	8	8	8	8
Formula weight	567.74	503.52	435.22	385.16
***A* U_{xx}** (Å^2)	0.054(1)	0.035(2)	0.016(1)	0.0112(4)
***A* U_{xy}** (Å^2)	-0.021(1)	-0.014(2)	-0.003(1)	-0.0027(4)
Ti U_{iso} (Å^2)	0.0070(5)	0.0057(1)	0.006(2)	0.005(2)
O (48f) U_{iso} (Å^2)	0.014(2)	0.0126(4)	0.005(2)	0.010(2)
O (8b) U_{iso} (Å^2)	0.035(2)	0.0167(1)	0.001(2)	0.008(2)
O (48f) x (Å^2)	0.3209(1)	0.3243(2)	0.3257(2)	0.3286(2)
11BM R_{wp} (%)	13.4	16.9	16.7	14.5
NOMAD Bank 3 R_{wp} (%)	5.9	10.1	–	8.9
NOMAD Bank 4 R_{wp} (%)	6.0	6.5	–	8.9
NOMAD Bank 5 R_{wp} (%)	5.8	7.3	–	6.1
Total R_{wp} (%)	8.7	10.7	16.7	9.1

Formula	$Bi_{1.49(1)}Ho_{0.51(1)}Ti_2O_7$	$Bi_{0.52(2)}Ho_{1.48(2)}Ti_2O_7$	$Ho_2Ti_2O_7$
Source	neutron	neutron	neutron
Temperature (K)	300	300	300
Space Group	$Fd\bar{3}m$ (#227)	$Fd\bar{3}m$ (#227)	$Fd\bar{3}m$ (#227)
a (Å)	10.282(3)	10.1561(7)	10.0852(2)
Volume a (Å^3)	1087.1(4)	1047.6(3)	1025.8(1)
Z	8	8	8
Formula weight	603.73	560.56	537.65
***A* U_{xx}** (Å^2)	0.061(1)	0.021(4)	0.010(2)
***A* U_{xy}** (Å^2)	-0.020(1)	-0.006(3)	-0.003(2)
Ti U_{iso} (Å^2)	0.006(4)	0.006(2)	0.004(2)
O (48f) U_{iso} (Å^2)	0.017(2)	0.012(5)	0.0077(5)
O (8b) U_{iso} (Å^2)	0.033(2)	0.011(2)	0.0055(6)
O (48f) x (Å^2)	0.32193(2)	0.3268(4)	0.3286(4)
NOMAD Bank 3 R_{wp} (%)	8.5	5.5	6.7
NOMAD Bank 4 R_{wp} (%)	9.3	6.4	8.3
NOMAD Bank 5 R_{wp} (%)	8.2	6.0	6.4
Total R_{wp} (%)	8.5	5.8	6.9

Table 2: Refined crystallographic data at 2 K for the series $Bi_{2-x}RE_xTi_2O_7$ (RE^{3+}= Y, Ho) with the A-site cation in the ideal 16d position.

Formula	$Bi_{1.52(1)}Y_{0.48(1)}Ti_2O_7$	$Bi_{0.98(2)}Y_{1.02(2)}Ti_2O_7$	$Y_2Ti_2O_7$
Source	neutron	neutron	neutron
Temperature (K)	2	2	2
Space Group	$Fd\bar{3}m$ (#227)	$Fd\bar{3}m$ (#227)	$Fd\bar{3}m$ (#227)
a (Å)	10.2690(3)	10.2196(5)	10.0671(2)
Volume a (Å^3)	1082.89(4)	1067.30(20)	1020.27(5)
Z	8	8	8
Formula weight	567.74	503.52	385.16
***A* U_{xx}** (Å^2)	0.068(1)	0.043(2)	0.006(4)
***A* U_{xy}** (Å^2)	-0.030(1)	-0.018(2)	-0.0003(4)
Ti U_{iso} (Å^2)	0.002(5)	0.0010(1)	0.003(2)
O (48f) U_{iso} (Å^2)	0.013(2)	0.014(4)	0.006(2)
O (8b) U_{iso} (Å^2)	0.032(2)	0.018(1)	0.005(2)
O (48f) x (Å^2)	0.3209(1)	0.3246(2)	0.3290(2)
NOMAD Bank 3 R_{wp} (%)	6.5	8.0	9.8
NOMAD Bank 4 R_{wp} (%)	7.9	9.7	10.8
NOMAD Bank 5 R_{wp} (%)	6.5	9.0	8.1
Total R_{wp} (%)	6.8	8.7	9.3

Formula	$Bi_{1.49(1)}Ho_{0.51(1)}Ti_2O_7$	$Ho_2Ti_2O_7$
Source	neutron	neutron
Temperature (K)	2	2
Space Group	$Fd\bar{3}m$ (#227)	$Fd\bar{3}m$ (#227)
a (Å)	10.2730(3)	10.0751(2)
Volume a (Å^3)	1084.1(4)	1022.80(1)
Z	8	8
Formula weight	603.73	537.65
***A* U_{xx}** (Å^2)	0.066(1)	0.010(2)
***A* U_{xy}** (Å^2)	-0.028(1)	-0.003(2)
Ti U_{iso} (Å^2)	0.004(4)	0.003(2)
O (48f) U_{iso} (Å^2)	0.012(2)	0.009(5)
O (8b) U_{iso} (Å^2)	0.029(2)	0.0072(6)
O (48f) x (Å^2)	0.32193(2)	0.3288(4)
NOMAD Bank 3 R_{wp} (%)	8.7	6.0
NOMAD Bank 4 R_{wp} (%)	8.6	9.4
NOMAD Bank 5 R_{wp} (%)	10.8	7.0
Total R_{wp} (%)	8.8	8.6

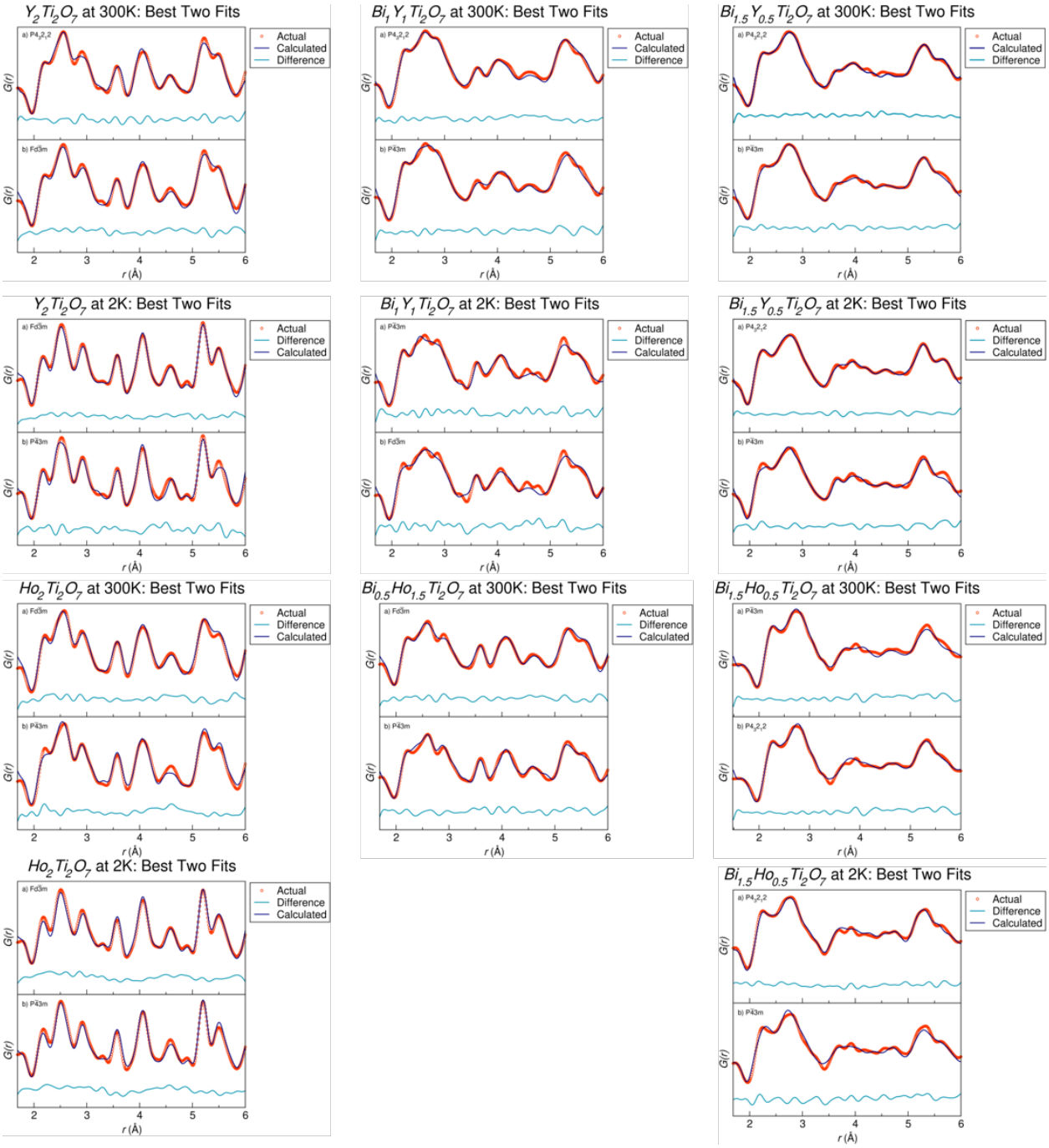

Figure 1: Fits of the neutron PDF (NOMAD, SNS) data from 1.5-6.0 Å against the lowest R_w (best fitting) structural models for each sample.

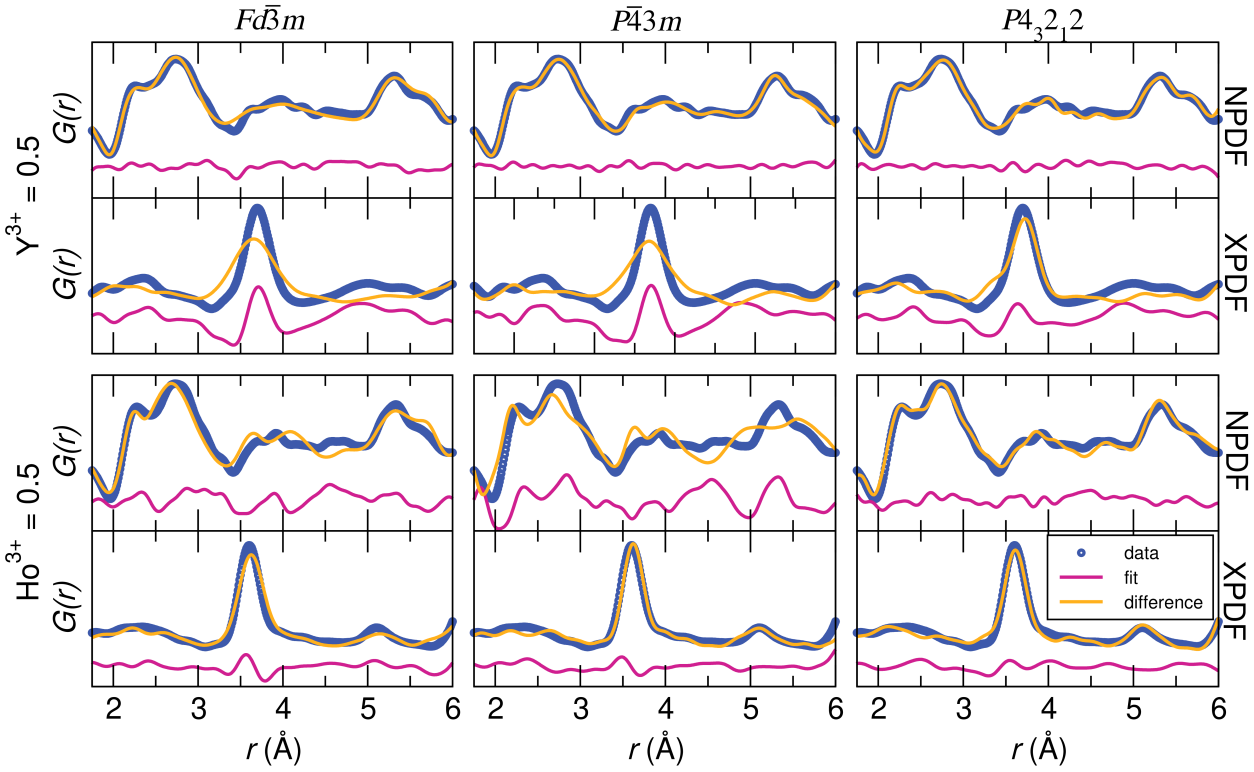

Figure 2: Fits (1.7-6.0 Å) from the joint analysis of the x-ray PDF (XPDF, PDF, NSLS-II) and neutron PDF (NPDF, NOMAD, SNS) data for $x = 0.5$ in $Bi_{2-x}RE_xTi_2O_7$ ($RE = Y^{3+}$, Ho^{3+}) samples against the three candidate structural models.

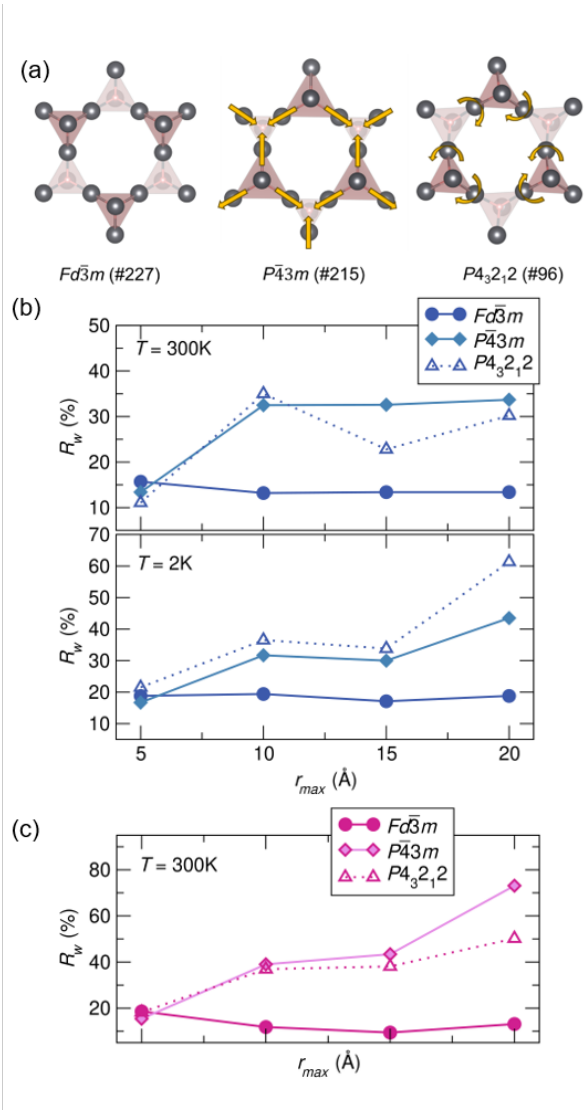

Figure 3: (a) Distortions of the A-site cations in the various structural models. R_w as a function of box-car r_{max} for (b) $Bi_{1.0}Y_{1.0}Ti_2O_7$ at 300 and 2 K and (c) $Bi_{0.5}Ho_{1.5}Ti_2O_7$ at 300 K (NPDF, NOMAD, SNS).

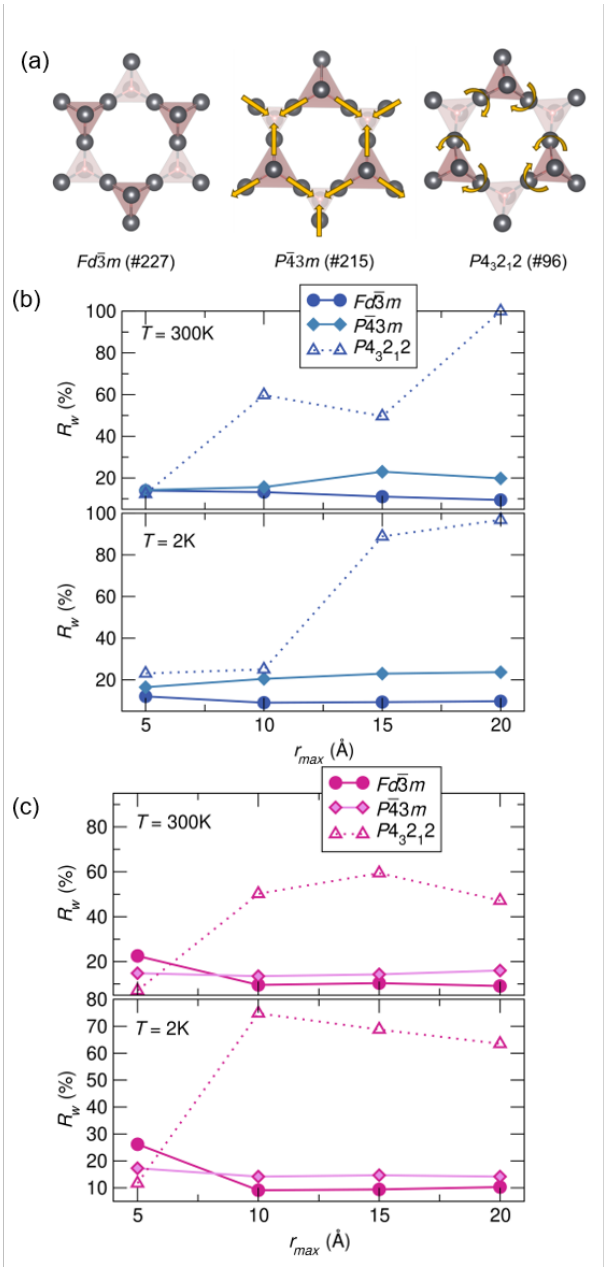

Figure 4: (a) Distortions of the A-site cations in the various structural models. R_w as a function of box-car r_{max} for (b) $Y_2Ti_2O_7$ at 300 and 2 K and (c) $Ho_2Ti_2O_7$ at 300 and 2 K (NPDF, NOMAD, SNS).

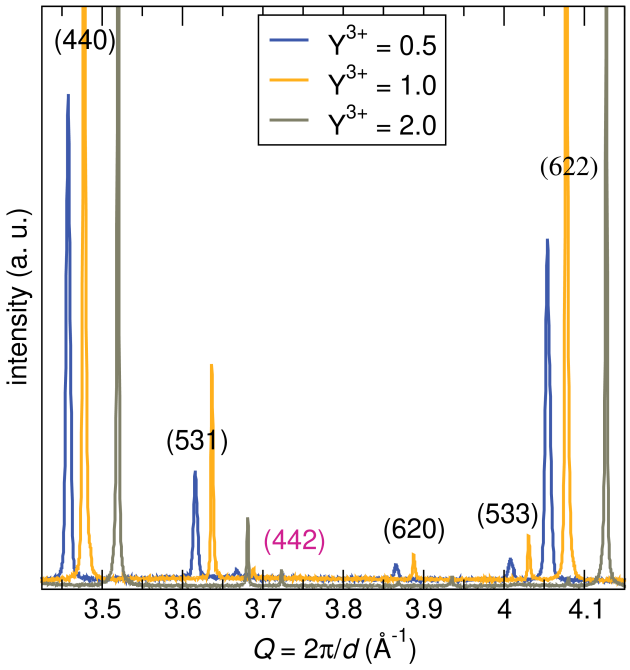

Figure 5: Section of the X-ray diffraction data (11BM, APS) showing the weak (442) reflection, hkl highlighted in pink.