Supporting Information for "Centrosymmetric to non-centrosymmetric transition in the $Ca_{2-x}Mn_xTi_2O_6$ double perovskite system studied through structural analysis and dielectric properties"

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Table I. Lattice parameters of $Ca_{2-x}Mn_xTi_2O_6$ for x =0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; and 1.0, determined by Rietveld refinement of powder XRD data. The amount of impurity phases was found to be less than 2%. Standard deviations for the lattice parameters are given in parentheses.

x	space group	a [Å]	b [Å]	c [Å]
0.2	$Pbnm$	5.36427(3)	5.43357(3)	7.63254(4)
0.3	$Pbnm$	5.38581(2)	5.39712(2)	7.6232(3)
0.4	$P4_2mc$	7.61263(3)		7.63618(5)
0.5	$P4_2mc$	7.59972(3)		7.64011(5)
0.6	$P4_2mc$	7.58661(3)		7.63863(4)
0.7	$P4_2mc$	7.58054(5)		7.63439(7)
0.8	$P4_2mc$	7.56404(3)		7.62478(4)
1.0	$P4_2mc$	7.54291(3)		7.60323(4)

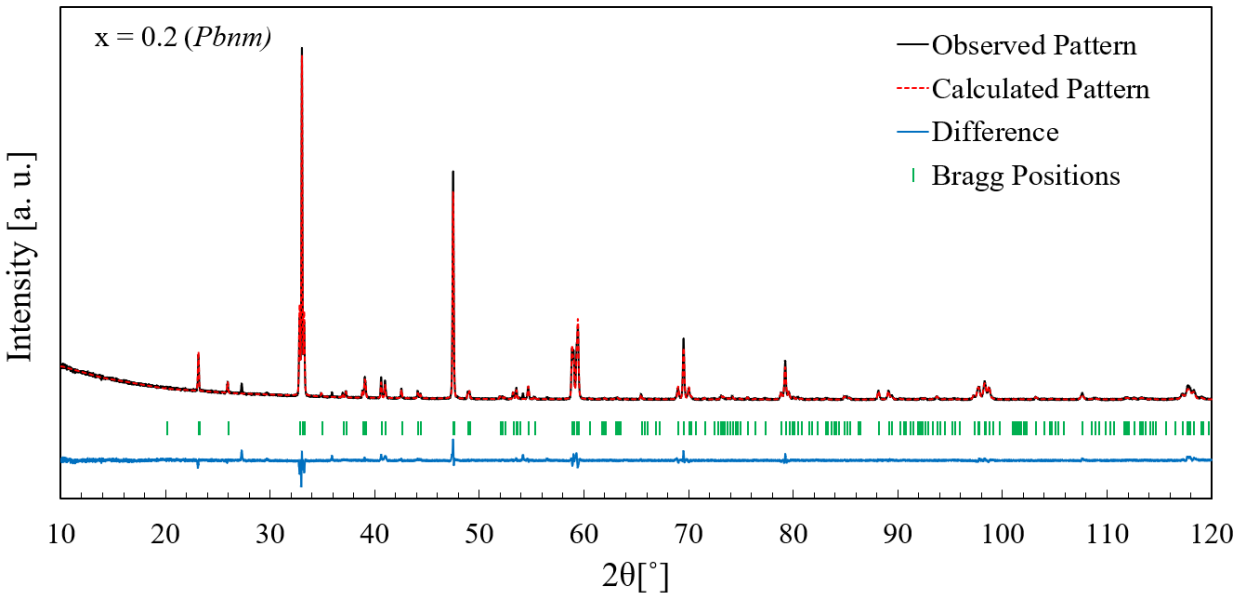

Figure 1. Rietveld refined powder X-ray diffraction pattern of $Ca_{2-x}Mn_xTi_2O_6$ ($x = 0.2$) in space group $Pbnm$. Measured pattern in black, calculated pattern in red, difference curve in blue, and Bragg positions in green. R_p: 8.39; R_{wp}: 11.3; χ^2: 4.25; R_{Bragg}: 8.97.

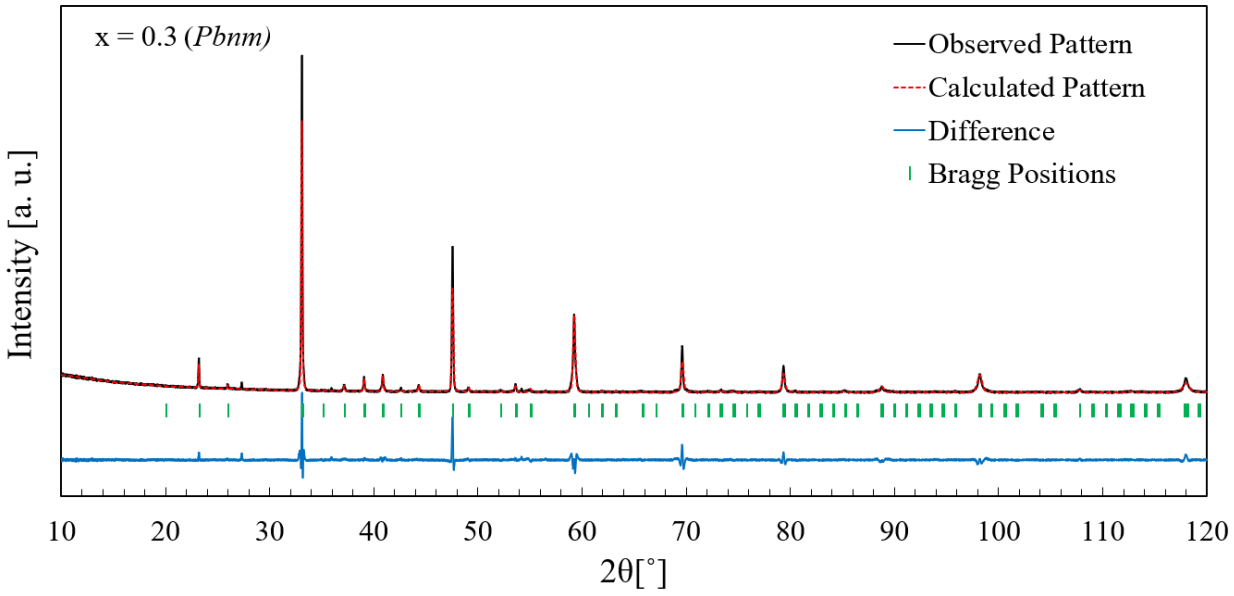

Figure 2. Rietveld refined diffraction pattern of $Ca_{2-x}Mn_xTi_2O_6$ with x = 0.3 in space group *Pbnm*. Measured pattern in black, calculated pattern in red, measured minus calculated pattern in blue, and the Bragg positions in green. R_p: 16.2; R_{wp}: 21.5; χ^2: 15.9; R_{Bragg}: 9.66.

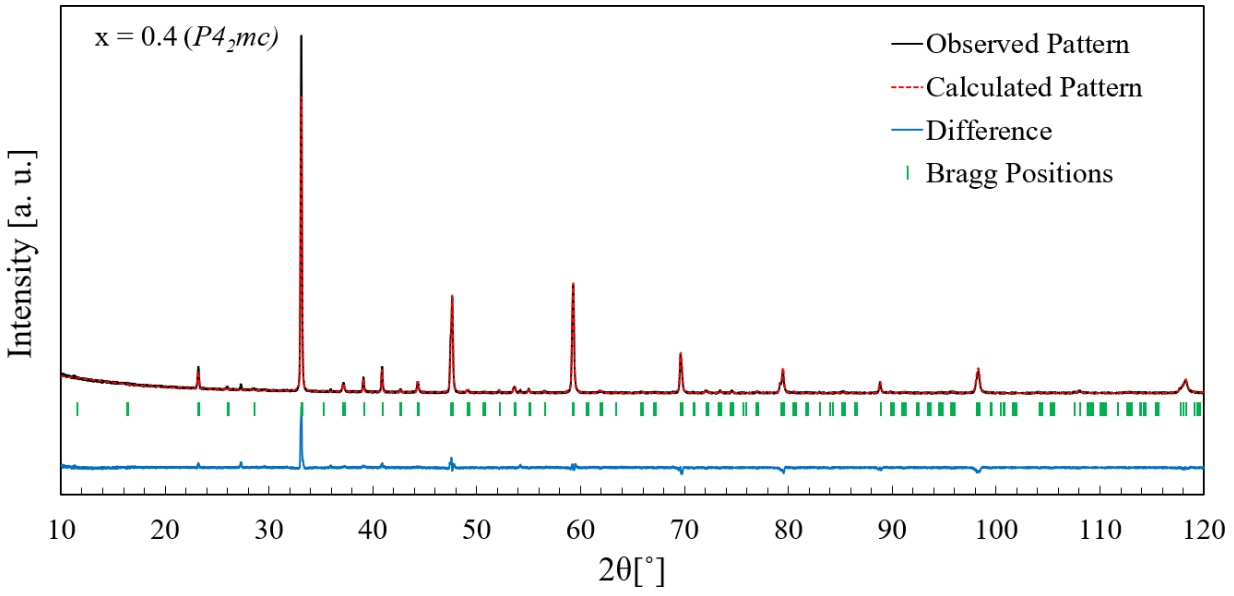

Figure 3. Rietveld refined diffraction pattern of $Ca_{2-x}Mn_xTi_2O_6$ with x = 0.4 in space group $P4_2mc$. Measured pattern in black, calculated pattern in red, measured minus calculated pattern in blue, and the Bragg positions in green. R_p: 10.4; R_{wp}: 13.9; χ^2: 9.20; R_{Bragg}: 15.2.

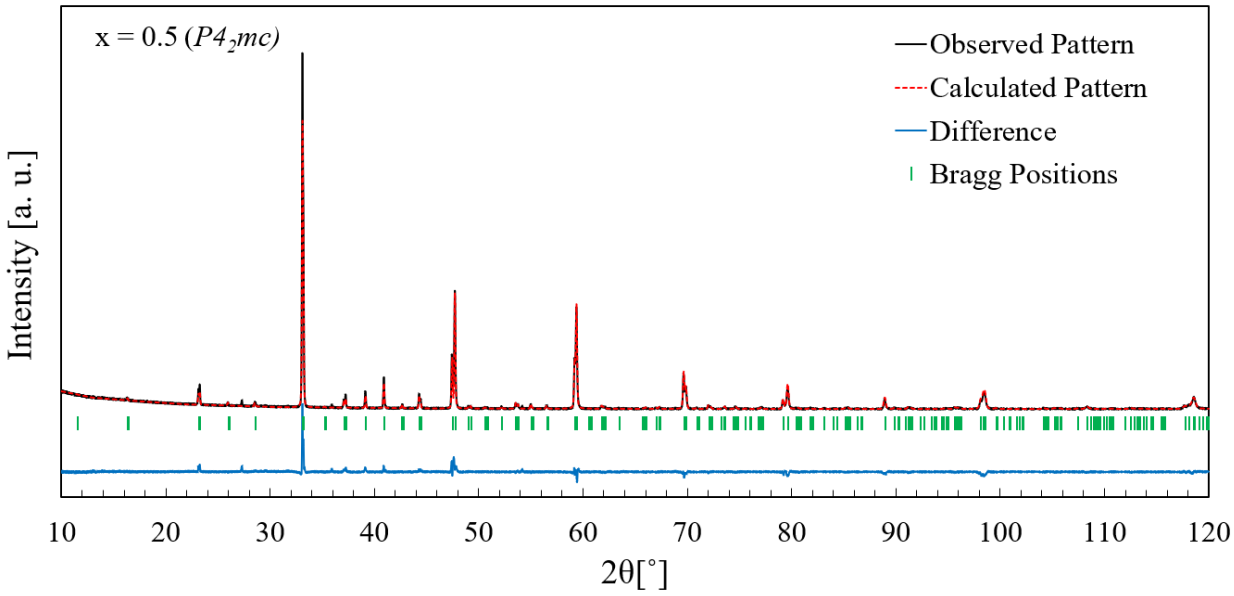

Figure 4. Rietveld refined diffraction pattern of $Ca_{2-x}Mn_xTi_2O_6$ with x = 0.5 in space group $P4_2mc$. Measured pattern in black, calculated pattern in red, measured minus calculated pattern in blue, and the Bragg positions in green. R_p: 11.2; R_{wp}: 14.9; χ^2: 11.1; R_{Bragg}: 15.5.

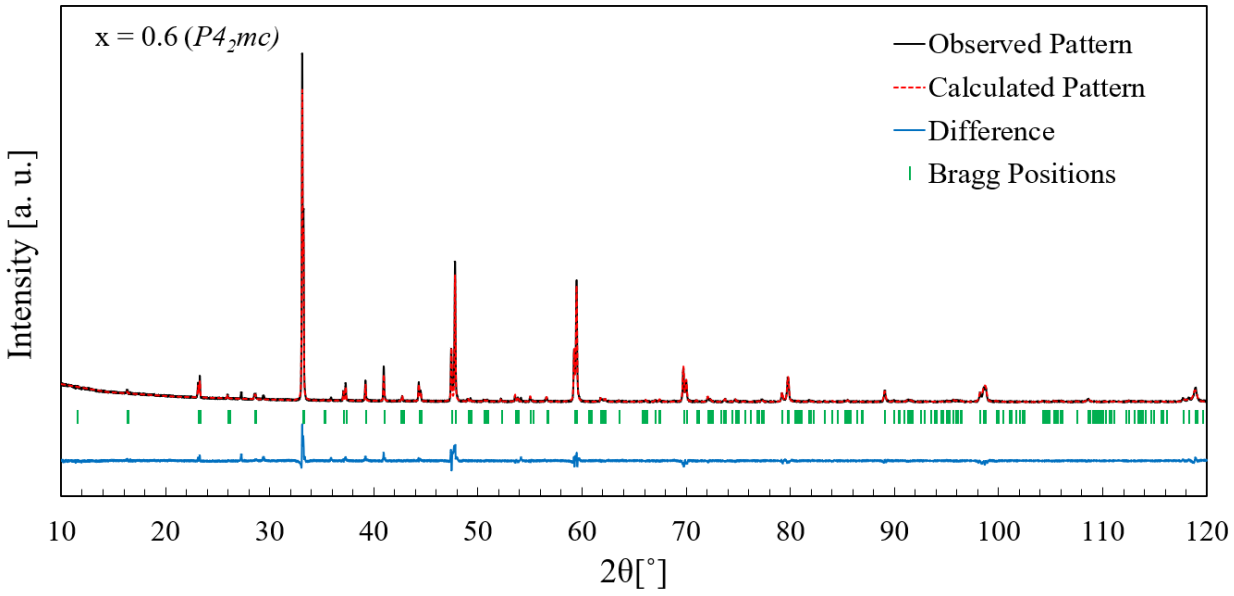

Figure 5. Rietveld refined diffraction pattern of $Ca_{2-x}Mn_xTi_2O_6$ with x = 0.6 in space group $P4_2mc$. Measured pattern in black, calculated pattern in red, measured minus calculated pattern in blue, and the Bragg positions in green. R_p: 11.2; R_{wp}: 15.1; χ^2: 10.6; R_{Bragg}: 10.0.

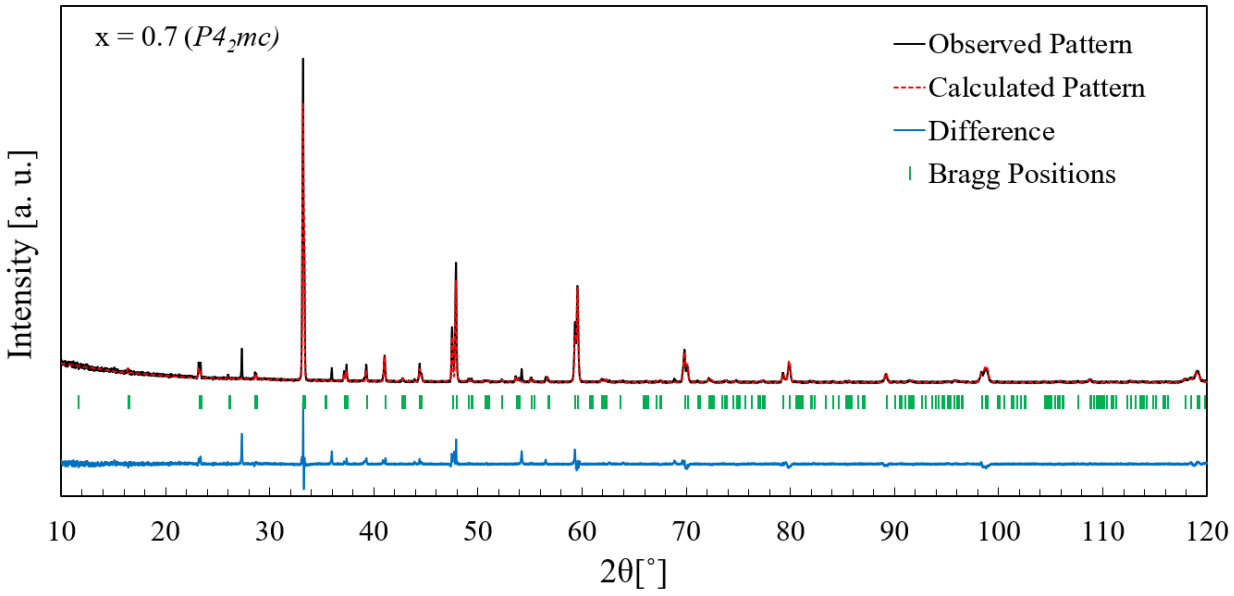

Figure 6. Rietveld refined diffraction pattern of $Ca_{2-x}Mn_xTi_2O_6$ with x = 0.7 in space group $P4_2mc$. Measured pattern in black, calculated pattern in red, measured minus calculated pattern in blue, and the Bragg positions in green. R_p: 14.2; R_{wp}: 19.2; χ^2: 3.74; R_{Bragg}: 17.1.

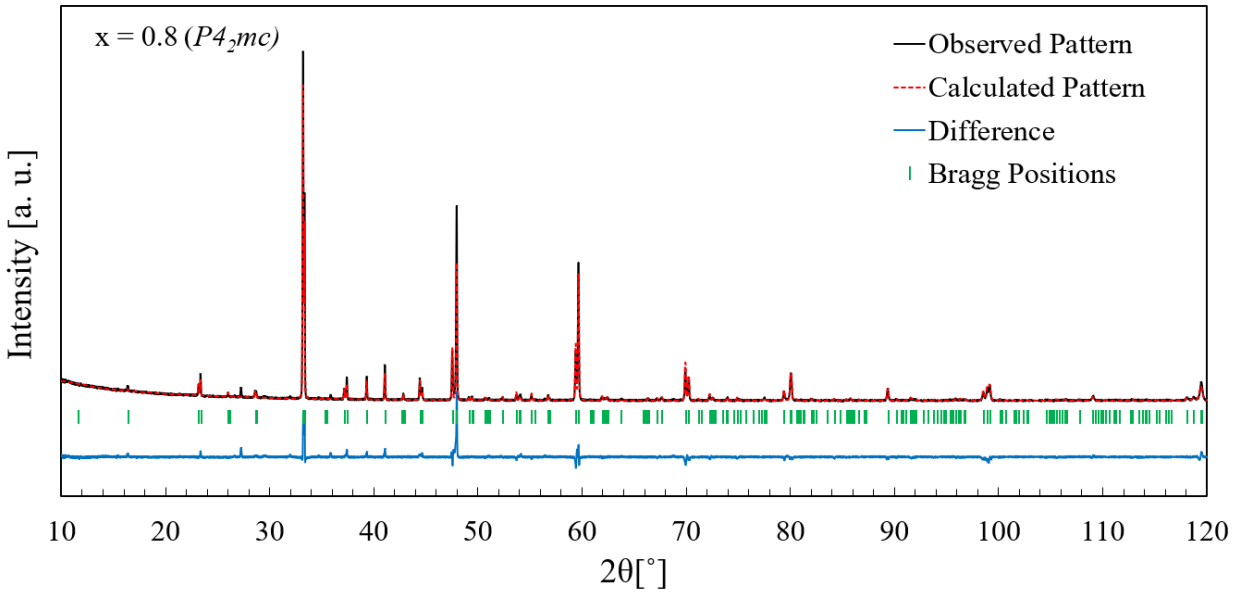

Figure 7. Rietveld refined diffraction pattern of $Ca_{2-x}Mn_xTi_2O_6$ with x = 0.8 in space group $P4_2mc$. Measured pattern in black, calculated pattern in red, measured minus calculated pattern in blue, and the Bragg positions in green. R_p: 13.3; R_{wp}: 17.9; χ^2: 13.0; R_{Bragg}: 14.7.

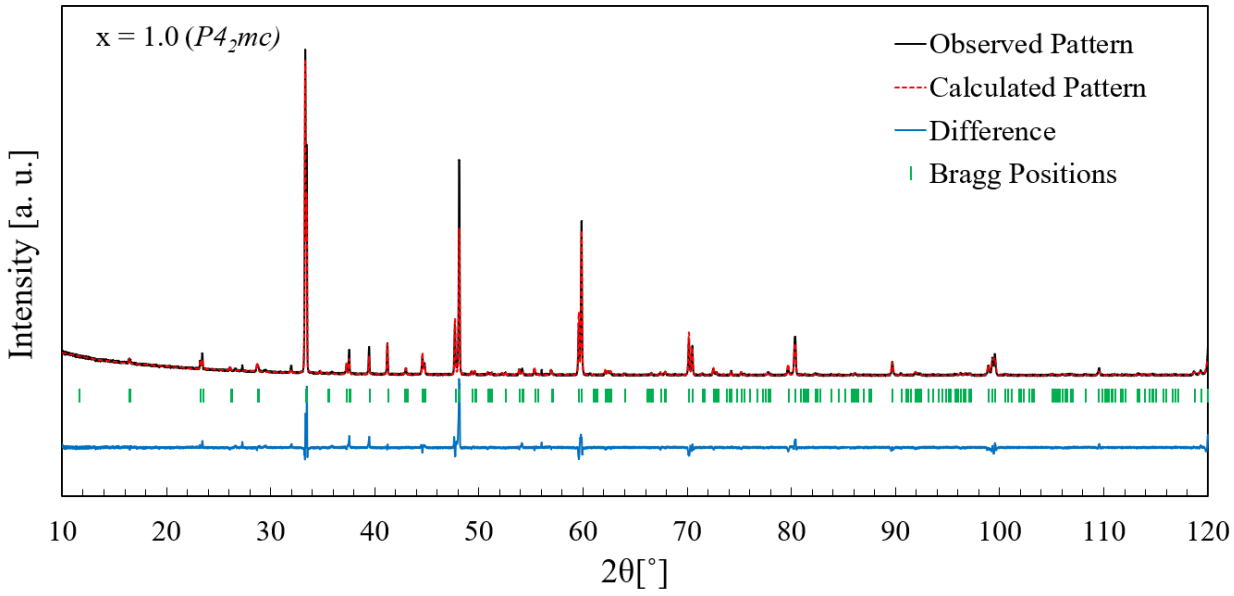

Figure 8. Rietveld refined diffraction pattern of $Ca_{2-x}Mn_xTi_2O_6$ with x = 1.0 in space group $P4_2mc$. Measured pattern in black, calculated pattern in red, measured minus calculated pattern in blue, and the Bragg positions in green. R_p: 11.6; R_{wp}: 16.6; χ^2: 12.5; R_{Bragg}: 13.9.

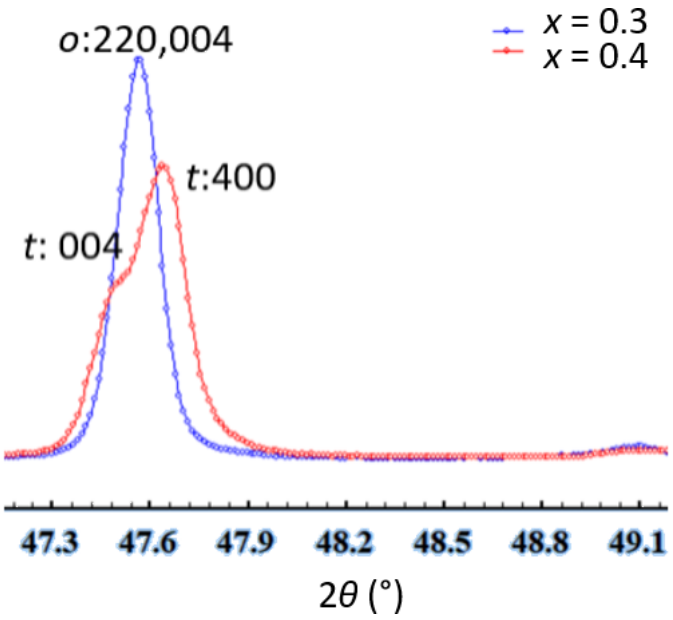

Figure 9. Diffraction pattern of $Ca_{2-x}Mn_xTi_2O_6$ with $x = 0.3$ (blue) and $x = 0.4$ (red). The peak belonging to an orthorhombic space group is marked with 'o' while the peaks belonging to a tetragonal unit cell are marked with 't'. The most general orthorhombic space group $Pmmm$ and the space group $Pbnm$ were used for 'o' and the most general tetragonal space group $P4/mmm$ and the space group $P4_2mc$ were used for 't'. While these space groups are the best fit for the peaks shown here, the peak splitting in $x = 0.4$ alone is not sufficient evidence for a tetragonal space group. The missing peak splitting for $x = 0.3$ arises from a fairly pseudo-cubic and highly pseudo-tetragonal unit cell.

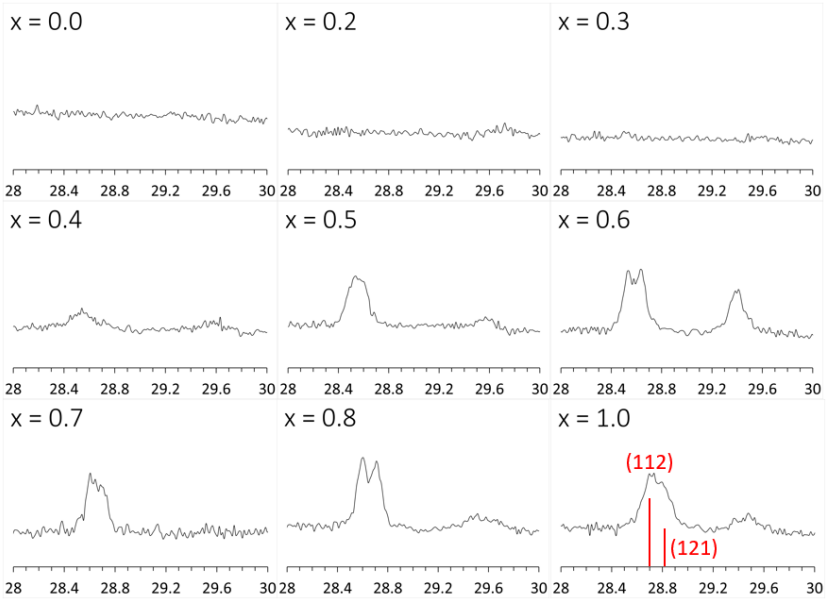

Figure 10. Changes around $2\theta = 28.8°$ in the powder diffraction pattern of $Ca_{2-x}Mn_xTi_2O_6$ from $CaTiO_3$ ($x = 0$) to $CaMnTi_2O_6$ ($x = 1$). The Miller indices of the peaks (112) and (121) appear only in the structure with the space group $P4_2mc$ and are given in red.

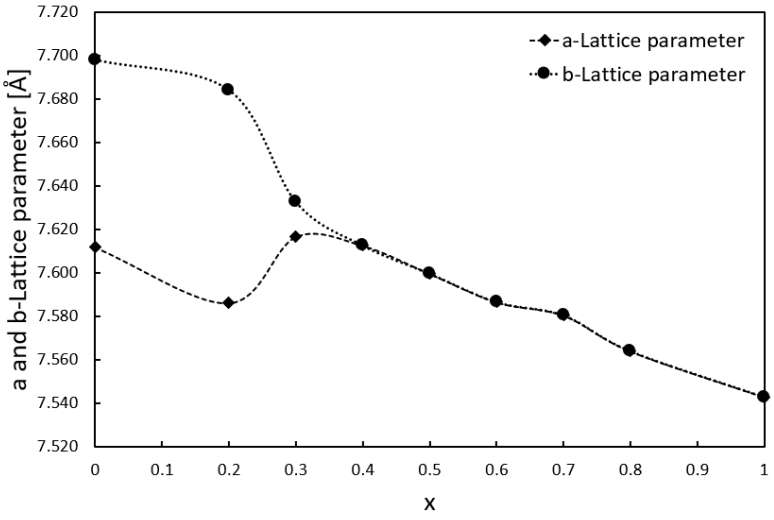

Figure 11. Relation between the lattice parameters a and b and the amount of Mn(II) substitution in $Ca_{2-x}Mn_xTi_2O_6$. The lattice parameters of those samples refined in space group $Pbnm$, $x = 0.0$ to 0.3 were scaled by a factor of $\sqrt{2}$.

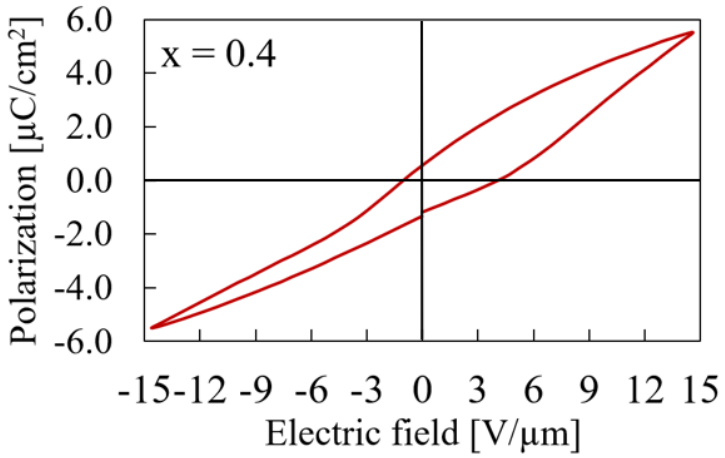

Figure 12. Polarization vs. electric field hysteresis curve of $Ca_{2-x}Mn_xTi_2O_6$ ($x = 0.4$) obtained with a maximum electric field of 15 V/μm at 20 Hz.

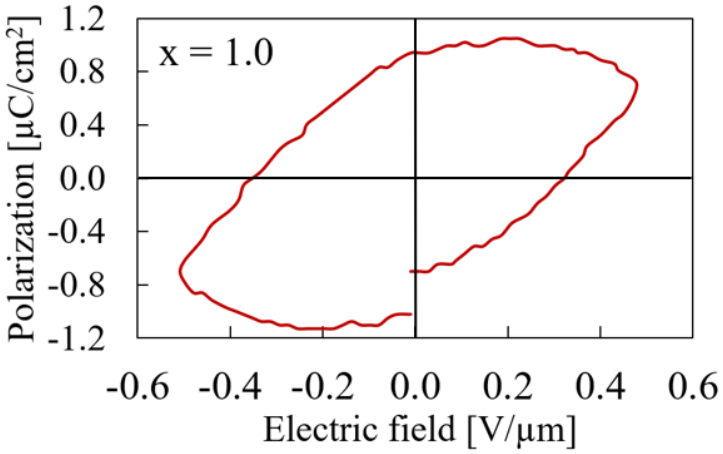

Figure 13. Polarization vs. electric field hysteresis curve of $Ca_{2-x}Mn_xTi_2O_6$ ($x = 1.0$) obtained with a maximum electric field of 0.5 V/μm at 20 Hz.