Supporting Information for Publication

A-Site and B-Site Charge Orderings in an *s*−*d* Level Controlled Perovskite Oxide $PbCoO_3$

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Supplementary Figures

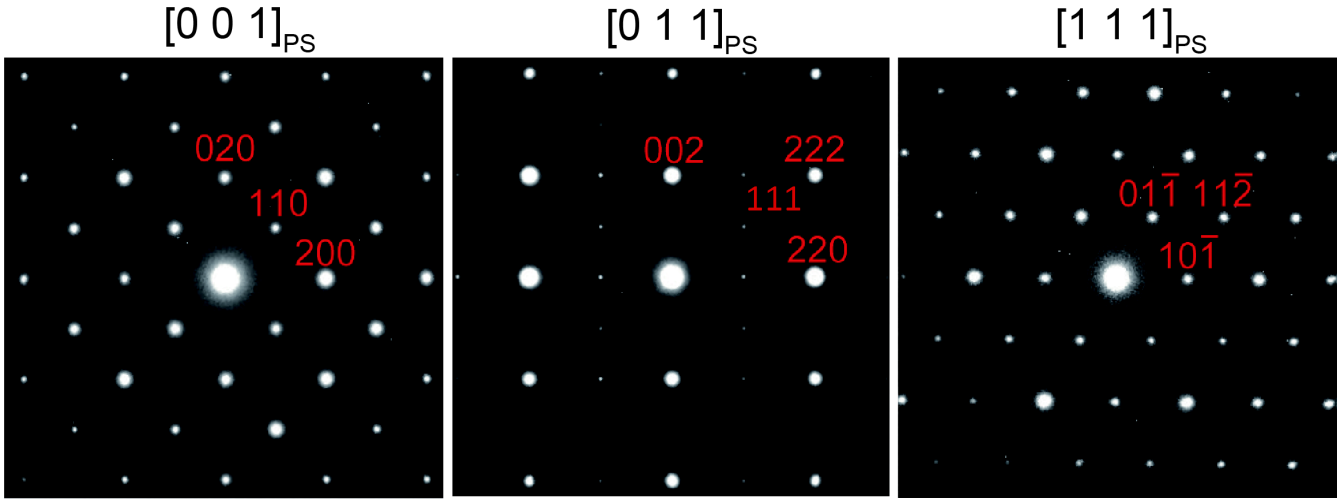

Figure S1 ED patterns along the [001], [011], and [111] zone axis at RT. The reflection conditions of o*kl* (*k* + *l* = 2n), *hhl* (any), and oo*l* (*l* = 2n) indicated the *Pn*-3 space group.

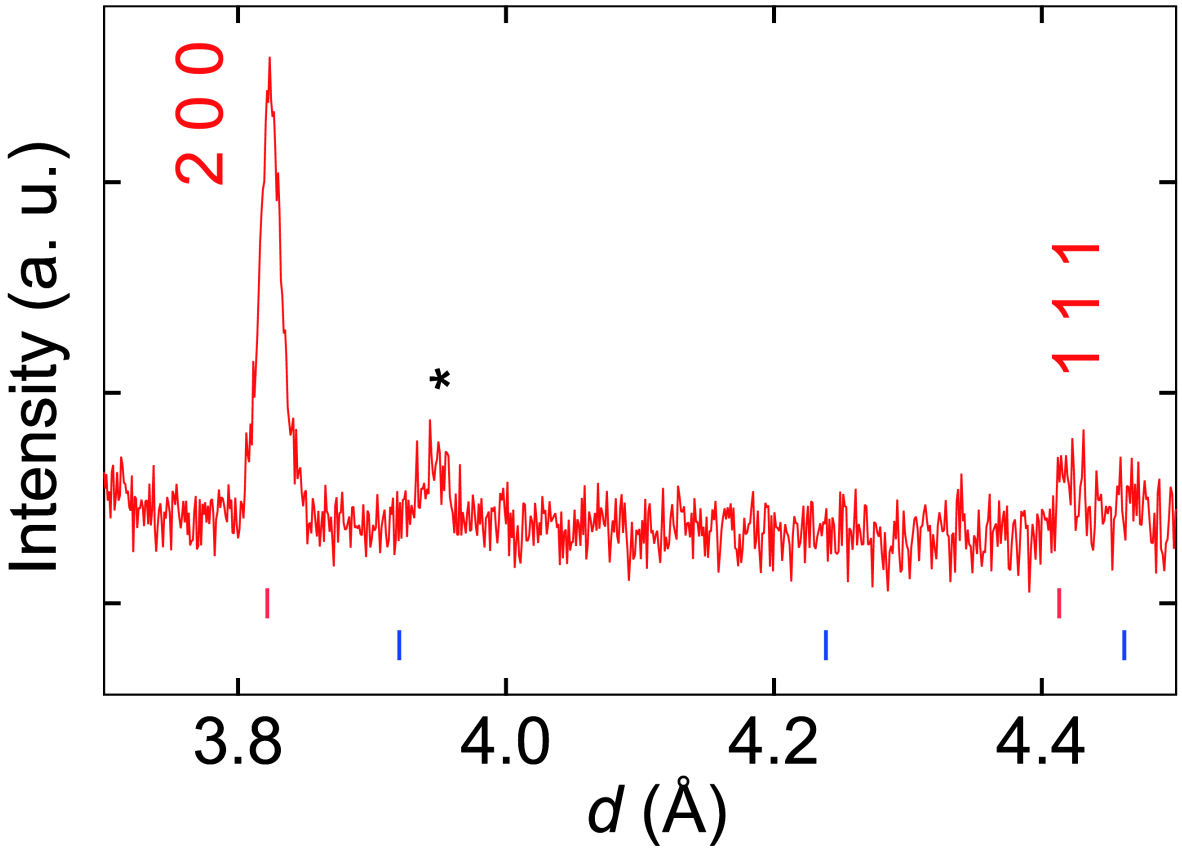

Figure S2 The magnified view of NPD patterns at RT. (111) super lattice reflection which is characteristic for *Pn*-3 structure is also observed. The tick marks correspond to the positions of Bragg reflections of the *Pn*-3 cubic phase (red), a $Pb_3(CO_3)_2(OH)_2$ impurity (blue). An asterisk indicates the diffraction from unknown impurity.

Supplementary tables

Table S1 Comparison of the reliability factors in the Rietveld analysis of SXRD with respect to the cubic perovskite structures. *Pn*-3(U_{aniso}) indicate the *Pn*-3 structure model using anisotropic atomic displacement parameters in A'-site.

S. G.	*Pm*-3*m*	*Fm*-3*m*	*Im*-3	*Pn*-3	*Pn*-3(U_{aniso})
R_{wp} (%)	12.34	11.98	8.01	7.92	5.09
R_B (%)	13.57	12.71	4.74	4.67	3.85
S	6.80	6.61	4.42	4.36	2.83

Table S2 Structural parameters of $PbCoO_3$ refined from SXRD patterns using the *Pn*-3 quadruple perovskite structure model.

	site	g	*x*	*y*	*z*	U_{iso} ($\times 10^{-2}$ Å^2)
Pb1	2*a*	1	1/2	1/2	1/2	0.55(3)
Pb2	6*d*	1	1/2	0	0	3.01*
Co1	4*b*	1	1/4	1/4	1/4	0.72(2)
Co2	4*c*	1	3/4	3/4	3/4	
O	24*h*	1	0.509(2)	0.316(1)	0.203(1)	1.27

Space group *Pn*-3 (No. 201), $Z = 2$, $a = 7.64998(4)$ Å, $V = 447.694(4)$ Å^3. * Equivalent isotropic atomic displacement parameters. Anisotropic atomic displacement parameters of Pb2 atom: $U_{11} = 1.76(8)\times 10^{-2}$ Å^2, $U_{22} = 6.40(9)\times 10^{-2}$ Å^2, $U_{33} = 0.86(6)\times 10^{-2}$ Å^2. The isotropic atomic displacement parameter of oxygen was fixed.

Table S3 Structural parameters of the calculated ground state of $PbCoO_3$ having *R*-3 symmetry with a lattice parameter $a = 7.683$ Å and a rhombohedral angle of 90.717°.

	Site	*x*	*y*	*z*
Pb^{2+}	2*c*	0.73999	0.73999	0.73999
Pb^{4+}	6*f*	0.25625	0.74942	0.20870
Co^{3+}	3*d*	$^1/_2$	0	0
Co^{3+}	1*b*	$^1/_2$	$^1/_2$	$^1/_2$
Co^{2+}	3*e*	0	$^1/_2$	$^1/_2$
Co^{2+}	1*a*	0	0	0
O	6*f*	0.43979	0.75994	−0.04067
O	6*f*	0.45379	0.73917	0.56056
O	6*f*	0.06983	0.73791	−0.04065
O	6*f*	0.03476	0.76157	0.56608

Table S4 Structural parameters of the calculated $PbCoO_3$ having *Pn*-3 symmetry with a lattice parameter *a* = 7.65970 Å.

Atom	site	*x*	*y*	*z*
Pb1	2*a*	1/2	1/2	1/2
Pb2	6*d*	1/2	0	0
Co1	4*b*	1/4	1/4	1/4
Co2	4*c*	3/4	3/4	3/4
O	24*h*	0.48962	0.29980	0.19779

Table S5 Comparison of the energies of several referent structures of $PbCoO_3$ with respect to the calculated ground state structure with *R*-3 symmetry, expressed in eV/f.u. for a ferromagnetic spin alignment. The f.u. used in all the calculations was unified to $PbCoO_3$ to compare the energies between different structures.

Pm-3*m*	*Fm*-3*m*	*Im*-3	*Pn*-3	*R*-3
4.87	0.83	0.31	0.06	0

Table S6 Fitting results for Pb 4f HAXPES of $PbCoO_3$, $PbCrO_3$, $PbNiO_3$, and $PbTiO_3$.

Sample	Peak	Binding energy (eV)	Peak area	FWHM (eV)	$Pb^{4+}_{area}/Pb^{2+}_{area}$
$PbCoO_3$	$Pb^{4+}4f_{7/2}$	137.44(0)	0.58(1)	0.69(0)	1.45
	$Pb^{2+}4f_{7/2}$	137.98(1)	0.40(1)	1.75(2)	
	$Pb^{4+}4f_{5/2}$	142.30(0)	0.47(1)	0.69(1)	1.34
	$Pb^{2+}4f_{5/2}$	142.78(2)	0.35(1)	1.88(2)	
$PbCrO_3$	$Pb^{4+}4f_{7/2}$	137.34(0)	0.50(2)	0.74(1)	0.67
	$Pb^{2+}4f_{7/2}$	137.93(2)	0.75(2)	1.53(2)	
	$Pb^{4+}4f_{5/2}$	142.19(0)	0.40(2)	0.76(2)	0.66
	$Pb^{2+}4f_{5/2}$	142.81(2)	0.61(2)	1.56(2)	
$PbNiO_3$	$Pb^{4+}4f_{7/2}$	137.29(1)	1.13(1)	1.11(1)	
	$Pb^{4+}4f_{5/2}$	142.15(1)	0.94(1)	1.13(1)	
$PbTiO_3$	$Pb^{2+}4f_{7/2}$	138.91(1)	1.22(2)	1.38(2)	
	$Pb^{2+}4f_{5/2}$	143.76(1)	1.01(2)	1.43(3)	