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Thermally Activated Rotational Disorder in $CaMoO_4$ Nanocrystals

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Synthesis of $CaMoO_4$ Nanocrystals. $CaMoO_4$ nanocrystals were synthesized via a vapor diffusion sol–gel method described in detail elsewhere.[1,2] Briefly, $MoO_2(acac)_2$ (95%, Strem Chemicals, Inc.) was dissolved in a $Ca(OCH_2CH_2OCH_3)_2$ alkoxide solution (19–25 wt. % in methoxypropanol, Gelest, Inc.) in a 1:1 molar ratio. The resulting solution was exposed to a controlled flow of water vapor for 48 h at room temperature and atmospheric pressure. Diffusion of water vapor into the solution resulted in the formation of a highly contracted gel, which was subsequently aged under nitrogen atmosphere for 24 h at 80 °C. The resulting gel was collected, washed with absolute ethanol (3 × 10 mL), and vacuum dried at room temperature to recover an off-white fine powder consisting of $CaMoO_4$ nanocrystals. These exhibited quasispherical shape with an average diameter of 9.3 ± 2.7 nm, as determined by transmission electron microscopy analysis (N = 250).

Synchrotron X-ray Diffraction. X-ray diffraction patterns were collected at the 11–ID–B beamline of the Advanced Photon Source at Argonne National Laboratory. An incident photon energy of 90.484 keV (λ = 0.137024 Å) was employed. The sample was loaded in a Kapton tube and diffraction data were collected in transmission mode from 90–480 K at a rate of 6 K/min using the Oxford cryosystems cryostream 700 plus.

Rietveld Analysis. Rietveld structural refinements were carried out using the GSAS software.[3,4] Experimental data and atomic X-ray scattering factors were corrected for sample absorption and anomalous scattering, respectively. The average crystal structure of $AMoO_4$ nanocrystals was refined with the tetragonal $I4_1/a$ (no. 88) space group. The following parameters were refined: (1) scale factor, (2) background, which was modeled using a shifted Chebyschev polynomial function, (3) peak shape, which was modeled using a modified Thomson–Cox–Hastings pseudo-Voigt function,[5] (4) lattice constants (a and c), (5) fractional atomic coordinates of the oxygen atom (x_O, y_O, z_O), and (6) atomic anisotropic displacement parameters constrained by the site symmetry (U^{11} and U^{33} for Ca and Mo, and U^{11}, U^{22}, U^{33}, U^{12}, U^{13}, and U^{23} for O). The R_{wp} indicator was employed to assess the quality of the refined structural models.[6]

Pair Distribution Function Analysis. The pair distribution function $G(r)$ defined as:

$$G(r) = 4\pi r[\rho(r) - \rho_0] = (2 / \pi) \int_Q^{Q_{max}} Q[S(Q) - 1] \sin(Qr)\, dQ$$

was employed for structural analysis. Here, r is the radial distance, $\rho(r)$ and ρ_0 are the local and average atomic number density, respectively, and Q is the magnitude of scattering vector. The RAD software was employed to extract $G(r)$ from the raw diffraction data.[7] These were first corrected for background, sample absorption, and Compton scattering. Then, normalized structure functions $S(Q)$ were obtained. Finally, $S(Q)$ was Fourier-transformed to yield $G(r)$. A maximum scattering vector (Q_{max}) of 24.5 $Å^{-1}$ was employed in the Fourier transform. Structural refinements were carried out using the PDFgui software.[8] The local crystal structure of $CaMoO_4$ nanocrystals was refined with the tetragonal $I4_1/a$ space group. Fits of this structural model to the experimental PDFs were performed in the 1.5–13 Å interatomic distance range in order to account for all atom–atom pairs along the largest dimension of the unit cell. The following parameters were refined: (1) scale factor, (2) lattice constants (a and c), (3) fractional atomic

coordinates of the oxygen atom (x_O, y_O, z_O), and (4) atomic anisotropic displacement parameters constrained by the site symmetry (U^{11} and U^{33} for Ca and Mo, and U^{11}, U^{22}, U^{33}, U^{12}, U^{13}, and U^{23} for O). The R_w indicator was employed to assess the quality of the refined structural models.[9]

Figures and Tables

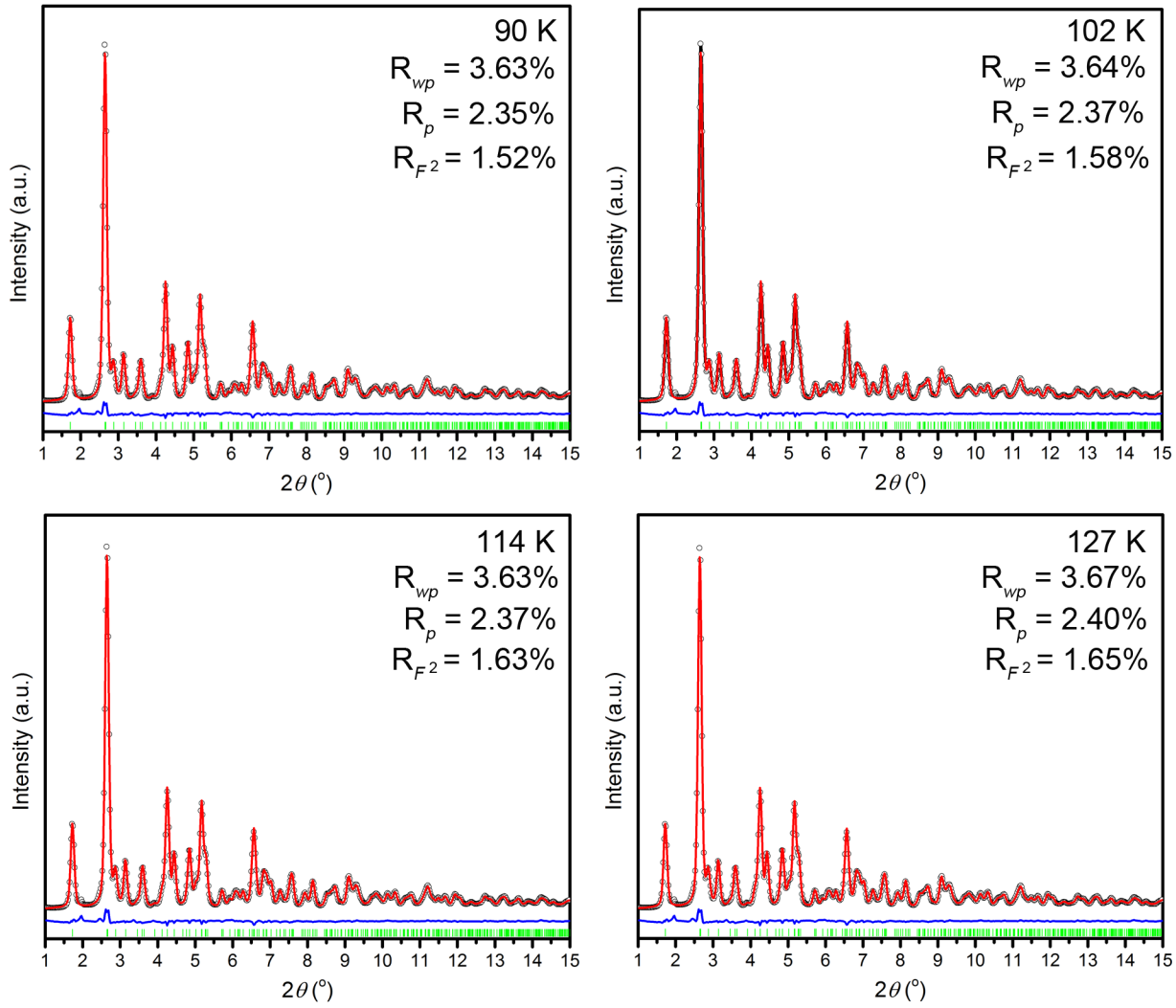

Fig. S1 Rietveld analysis of X-ray total scattering data for $CaMoO_4$ nanocrystals from 90–480 K. Experimental (○) and calculated (—) patterns are shown, along with the difference curve (—) and tickmarks (|) corresponding to the phase refined. The temperature at which the pattern was collected is indicated in the top right of each pattern, along with the associated R_{wp}.

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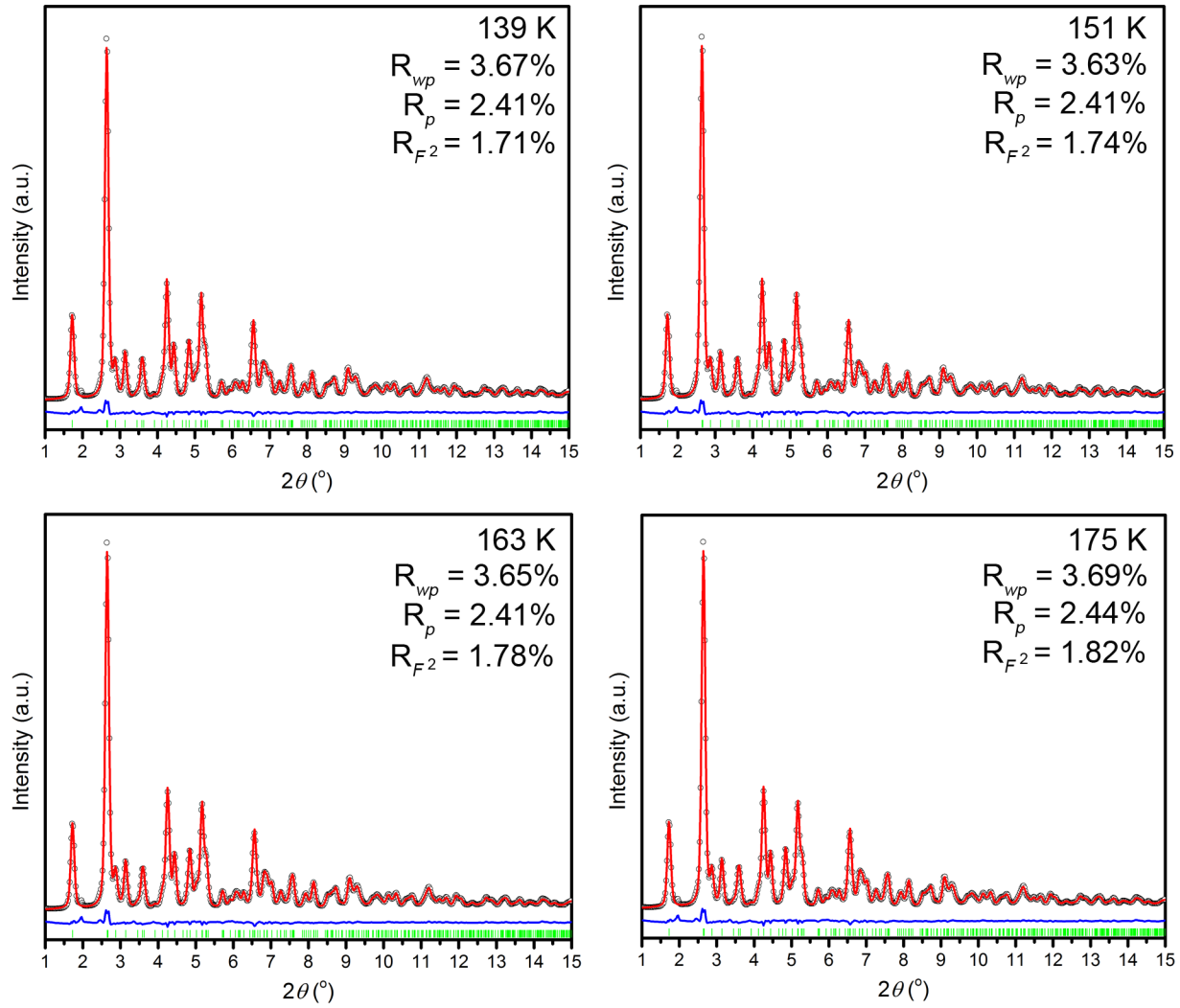

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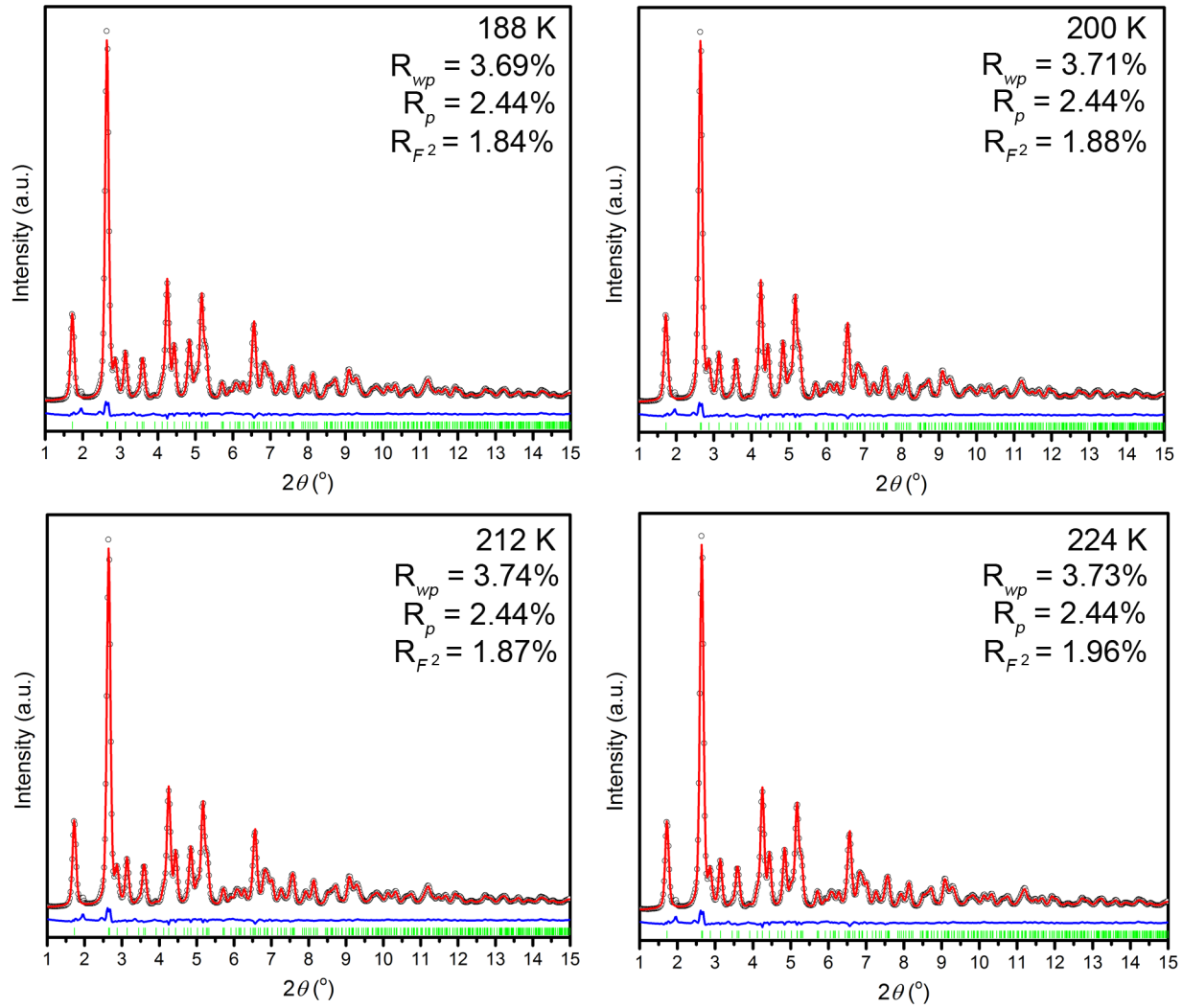

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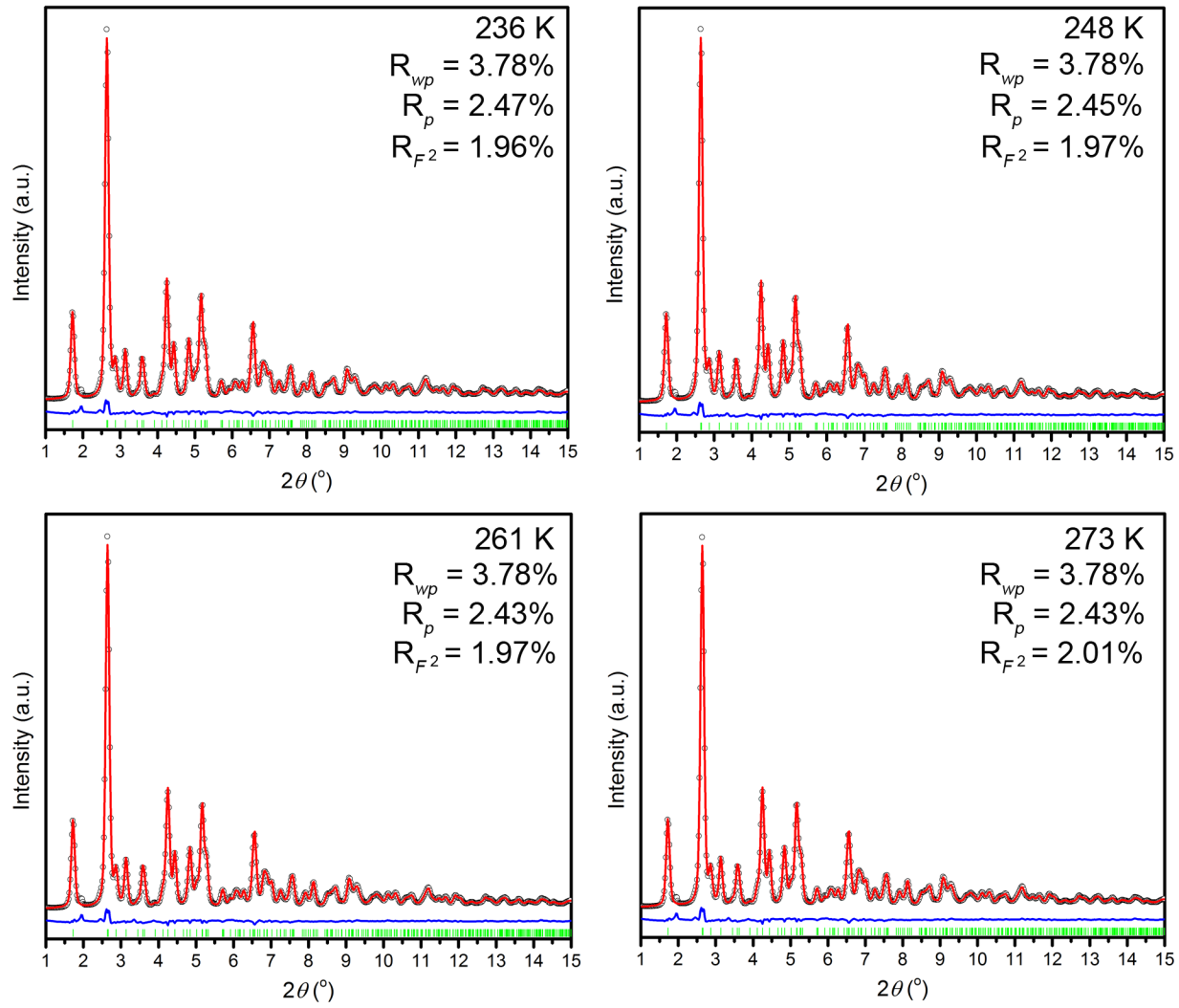

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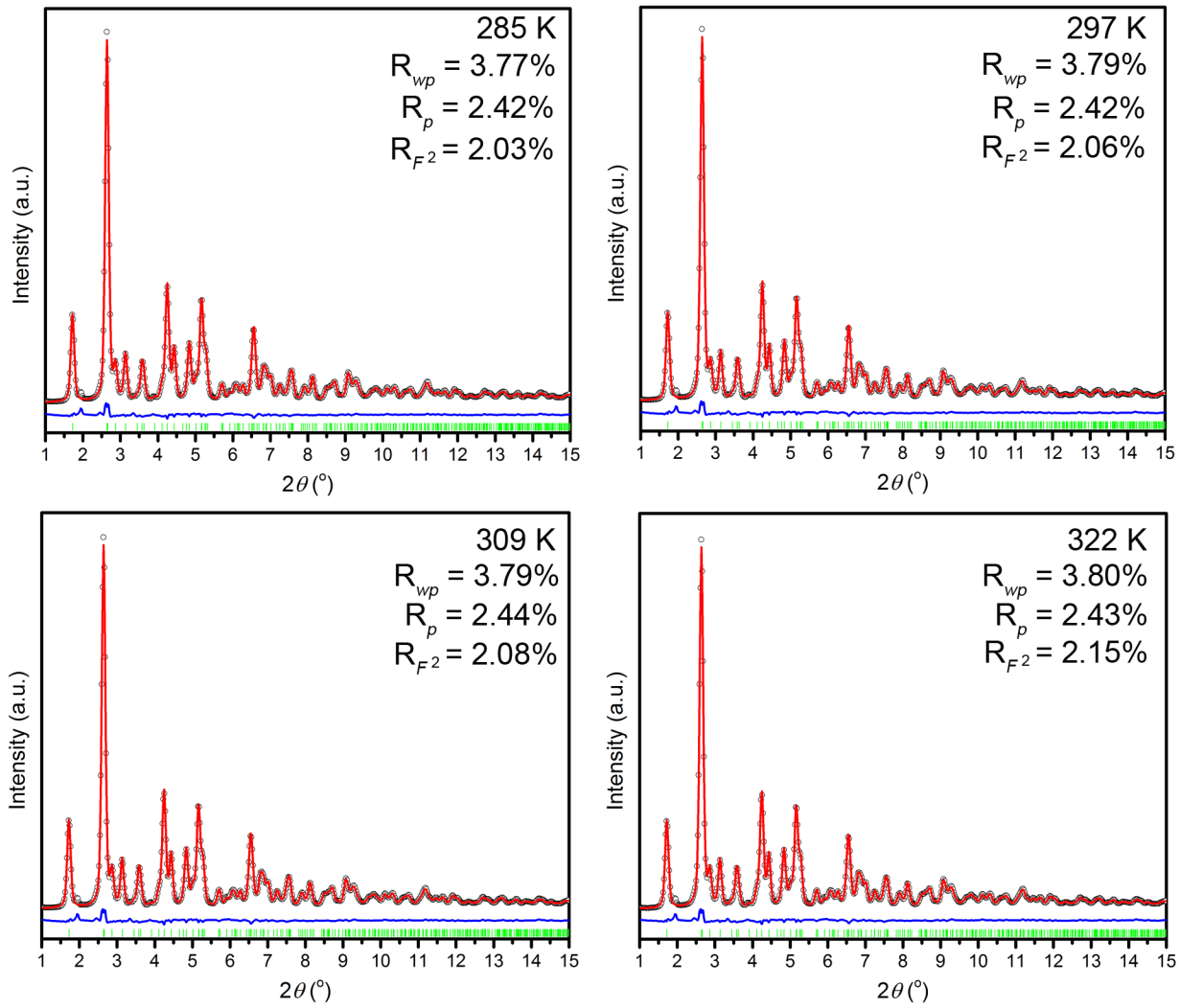

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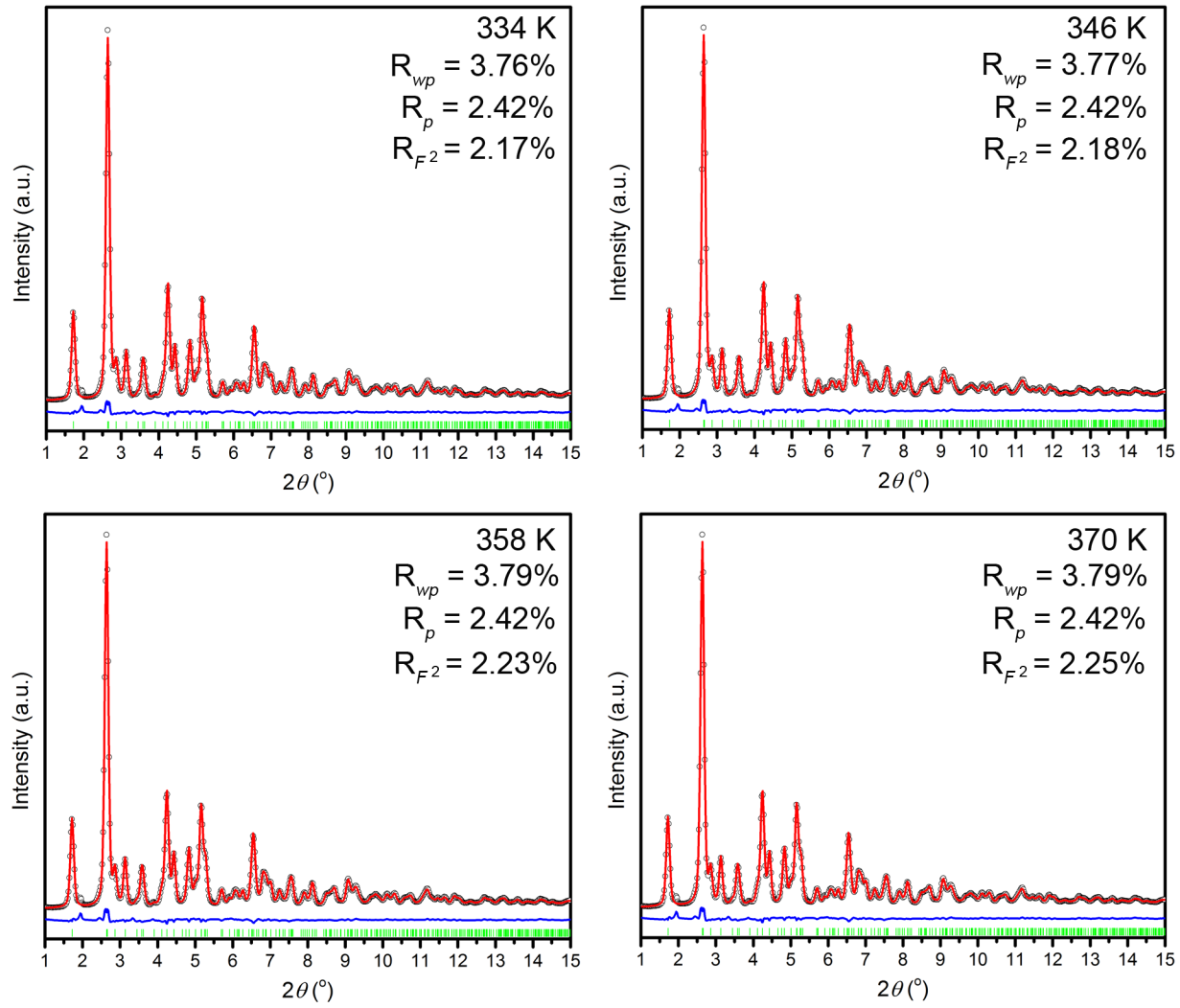

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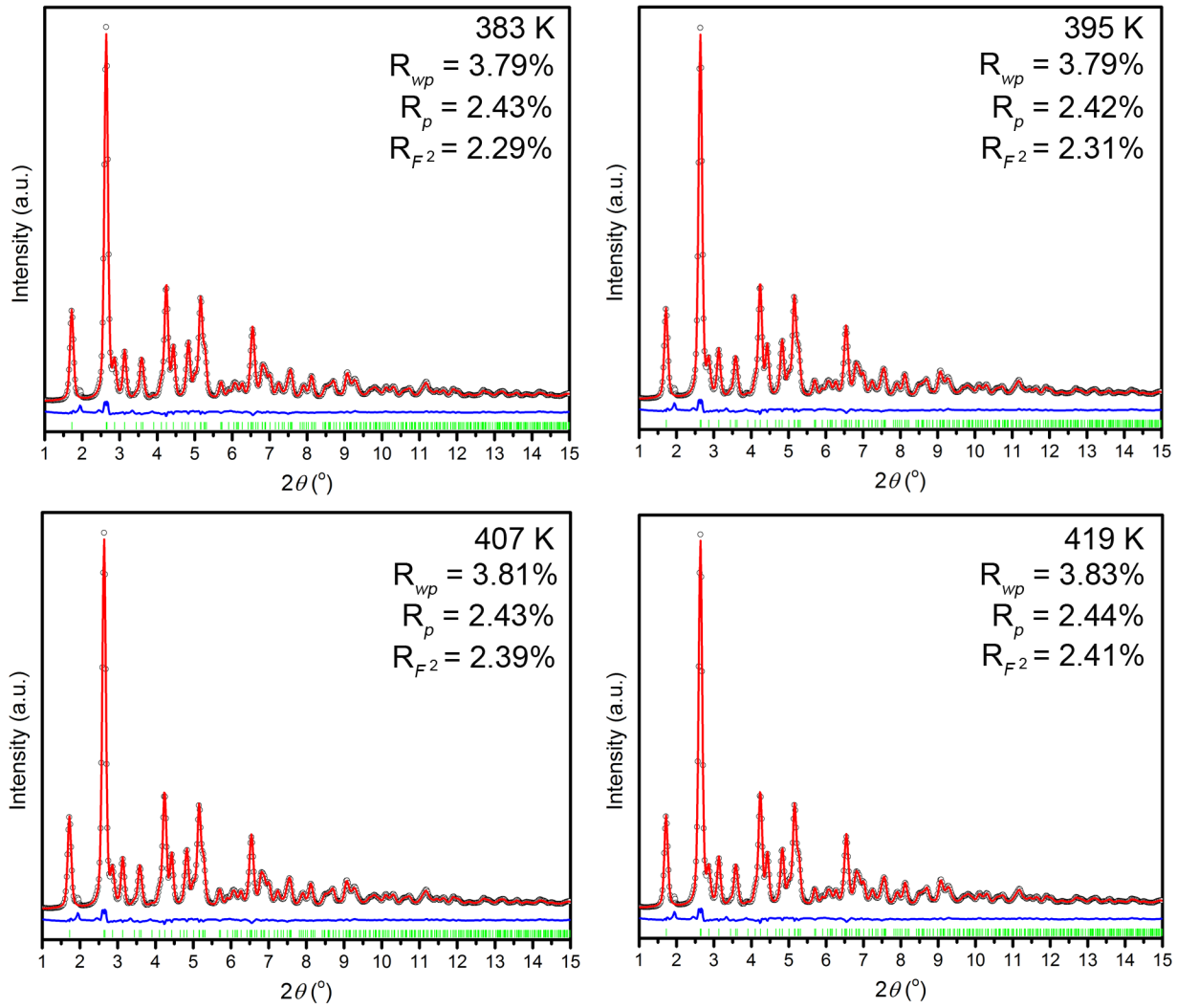

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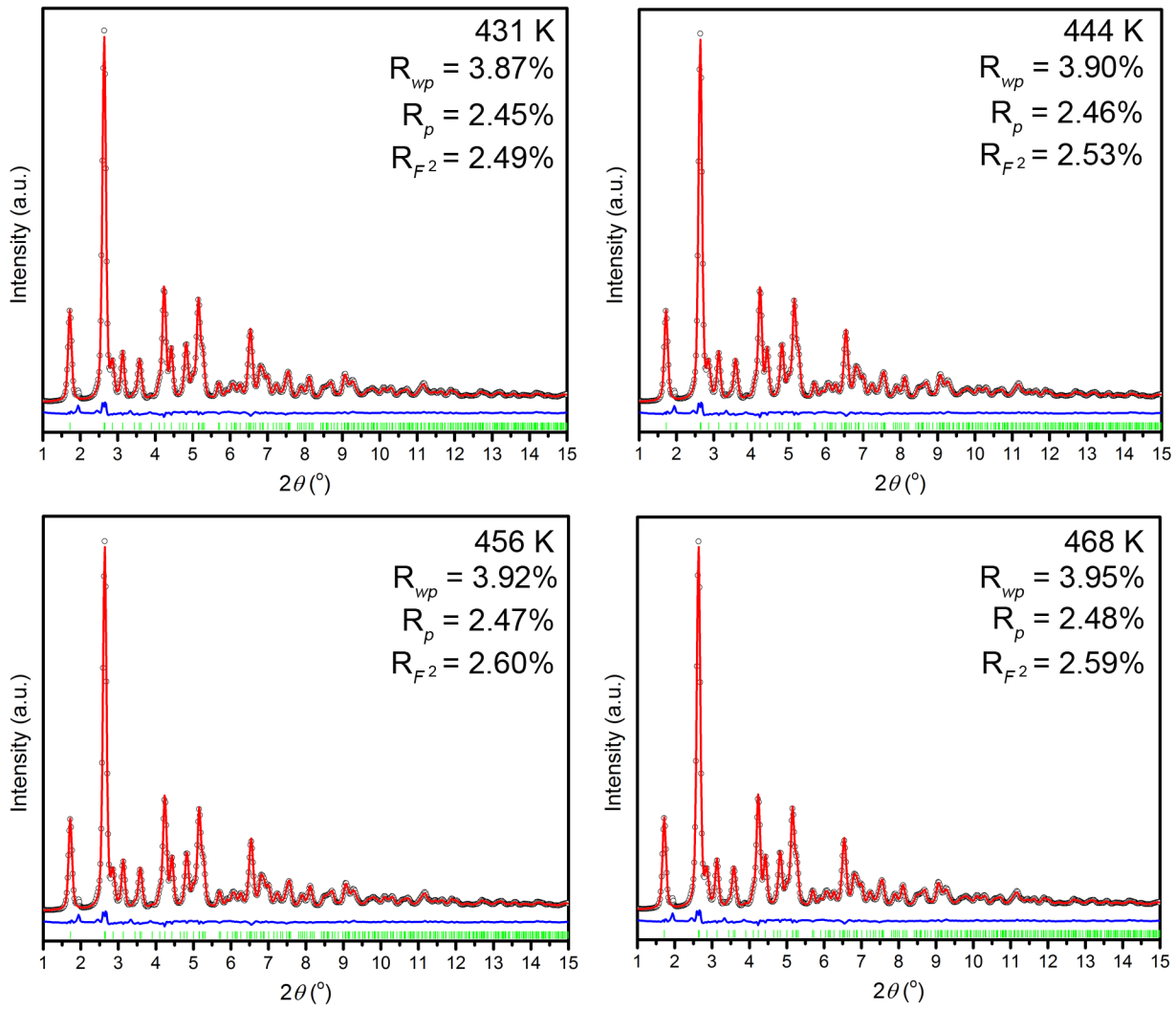

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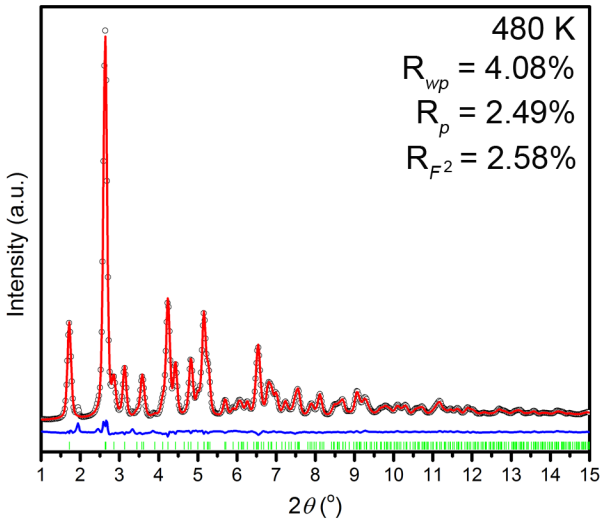

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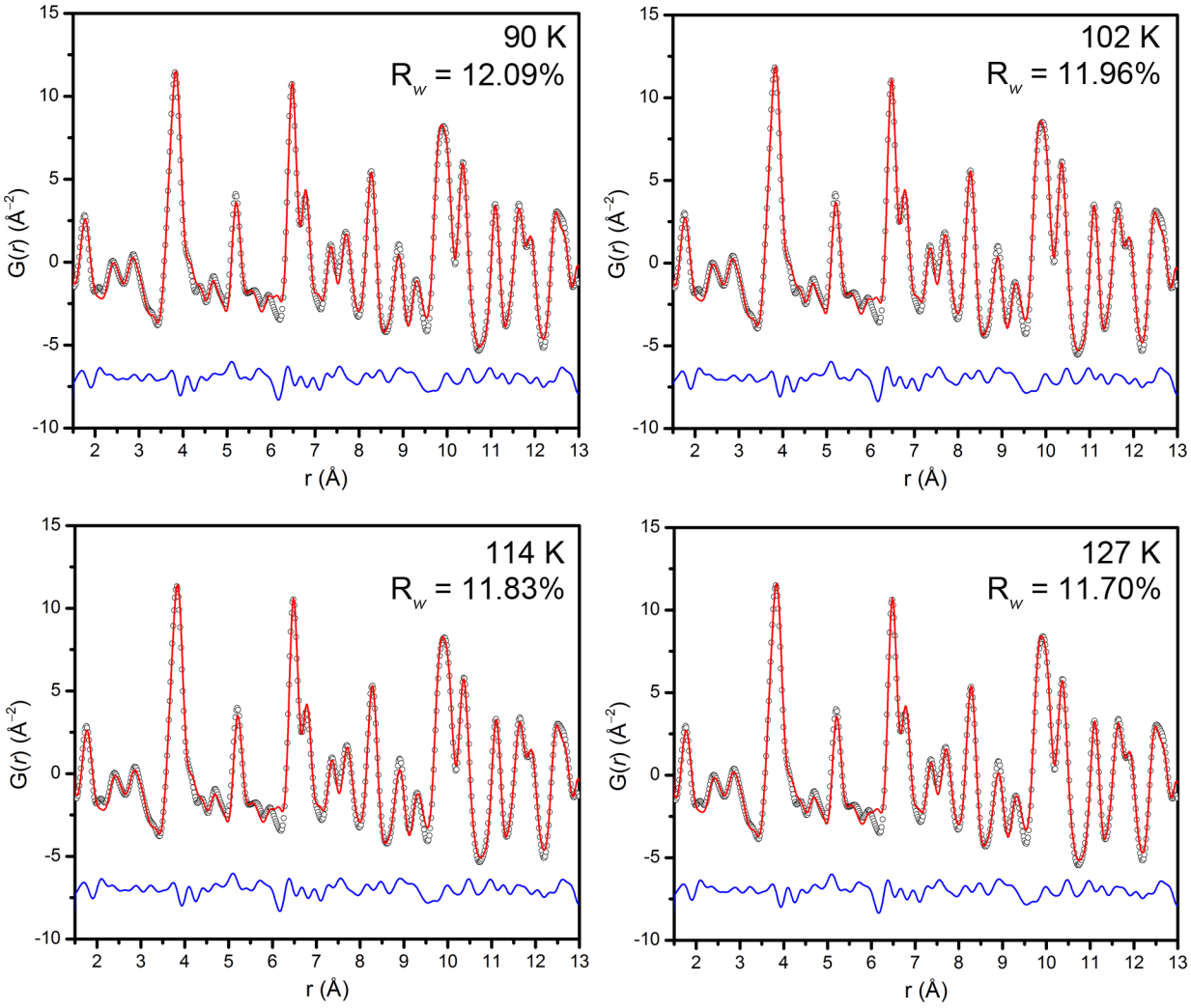
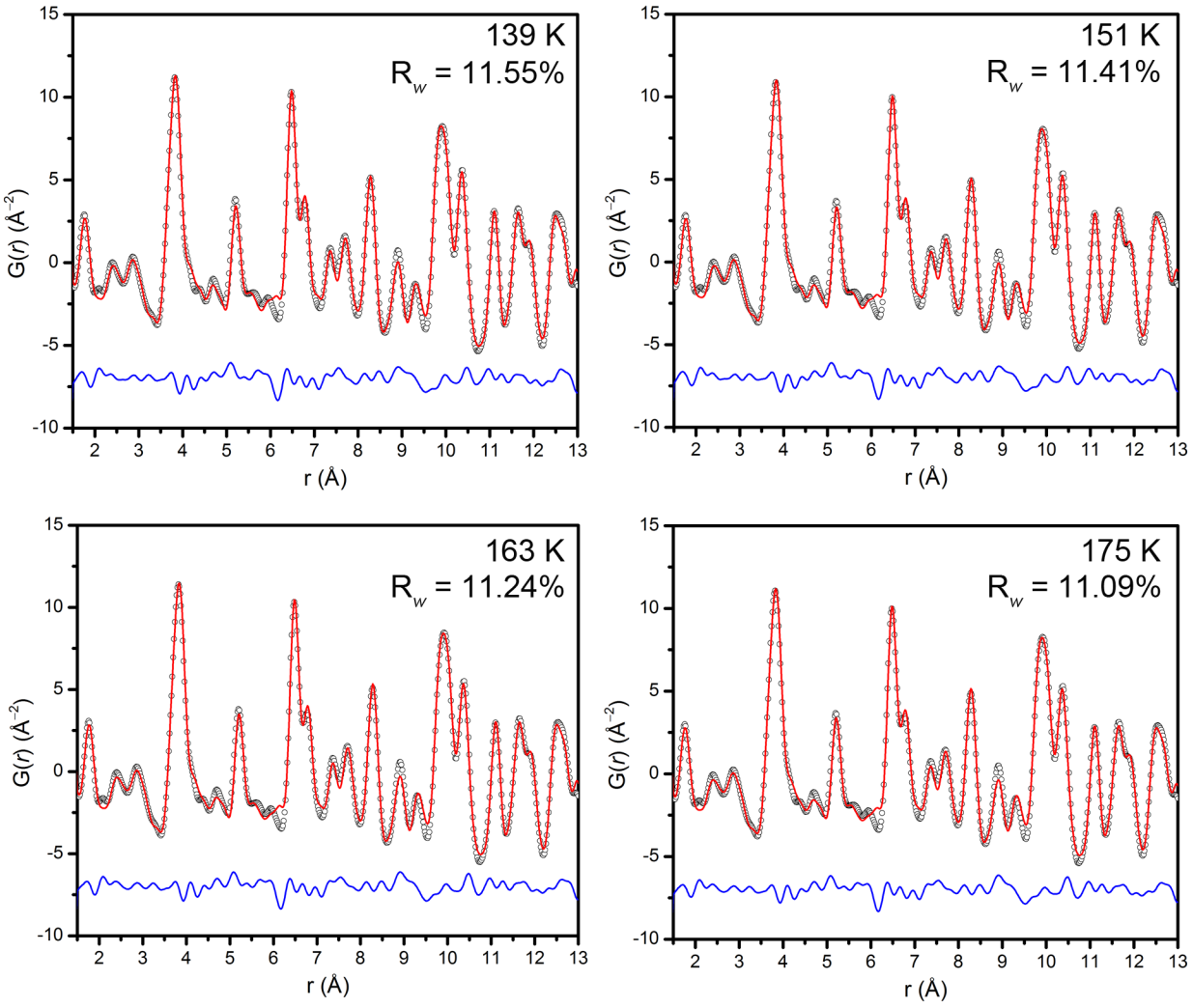


Fig. S2 PDF analysis of X-ray total scattering data for $CaMoO_4$ nanocrystals from 90–480 K. Experimental (○) and calculated (—) patterns are shown, along with the difference curve (—). The temperature at which the pattern was collected is indicated in the top right of each pattern, along with the associated R_w. —*Continues on the following page.*



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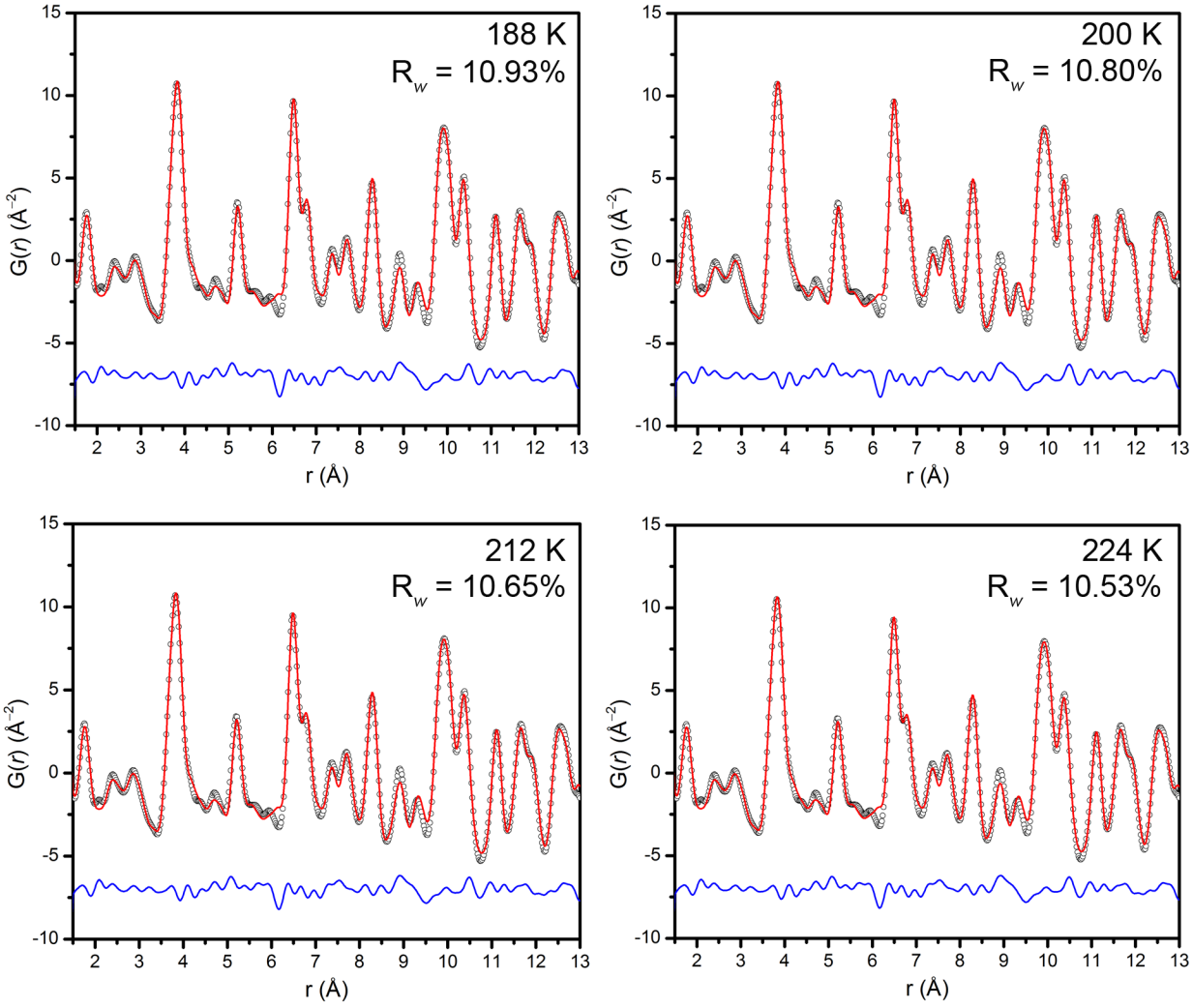

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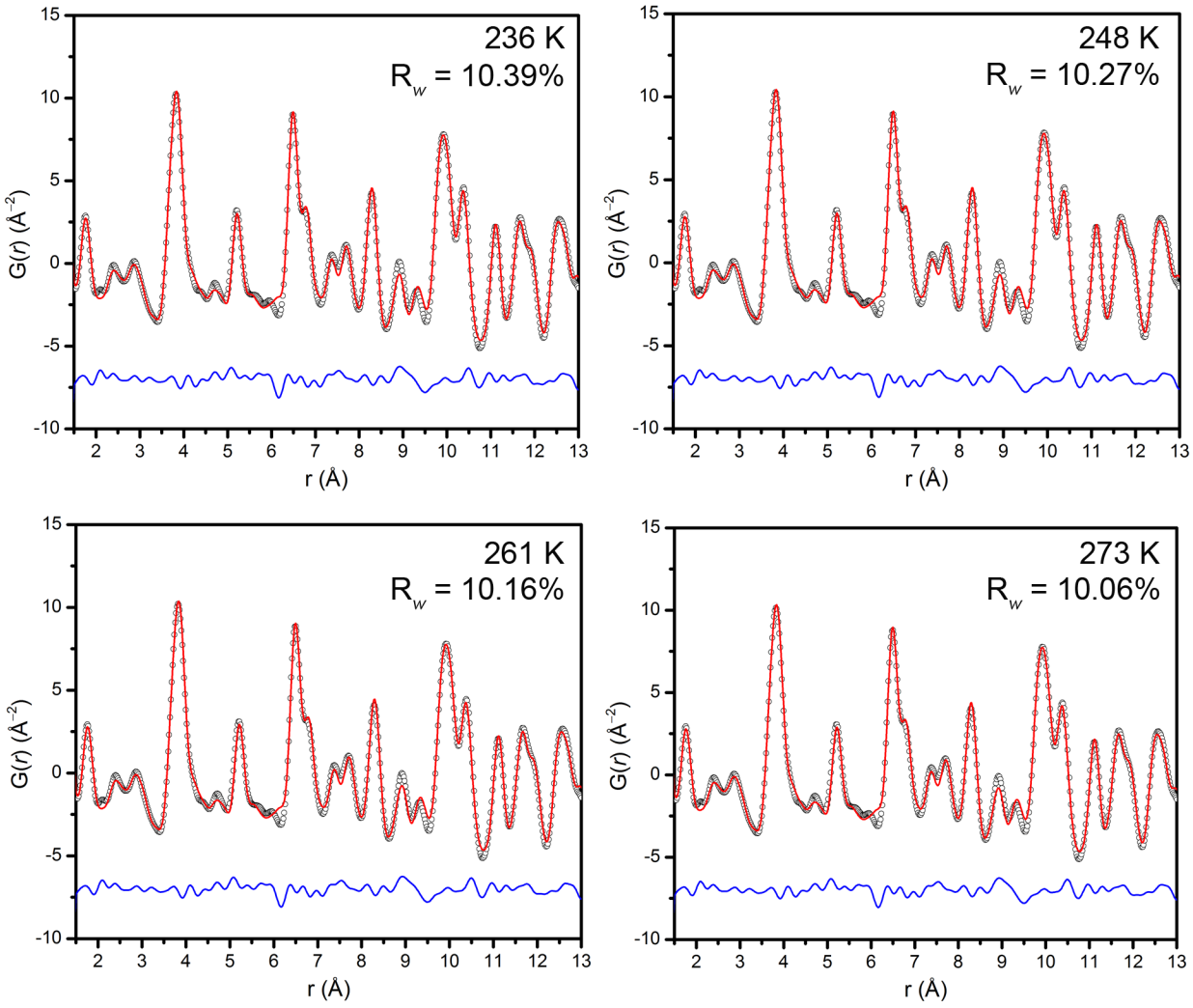

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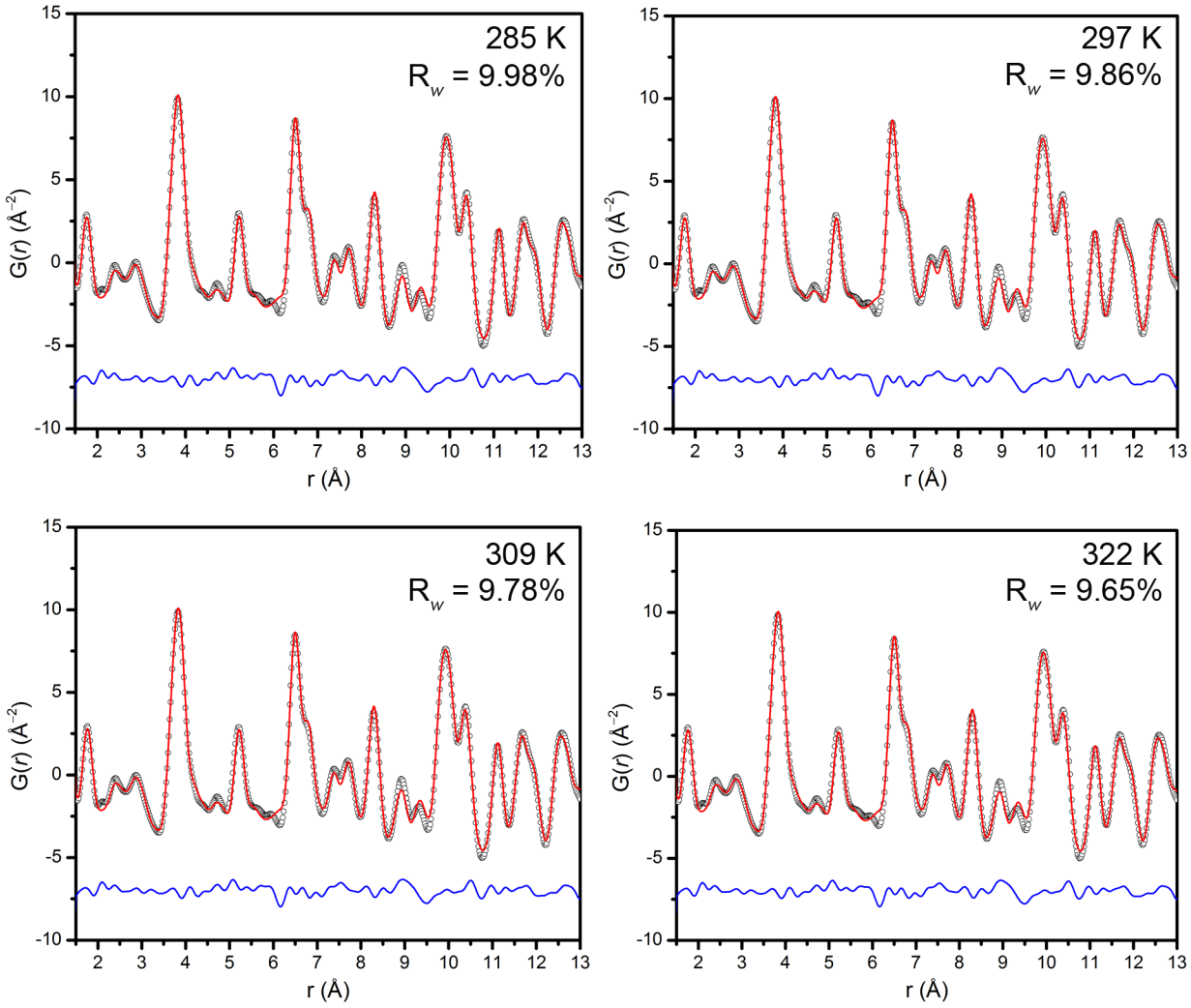

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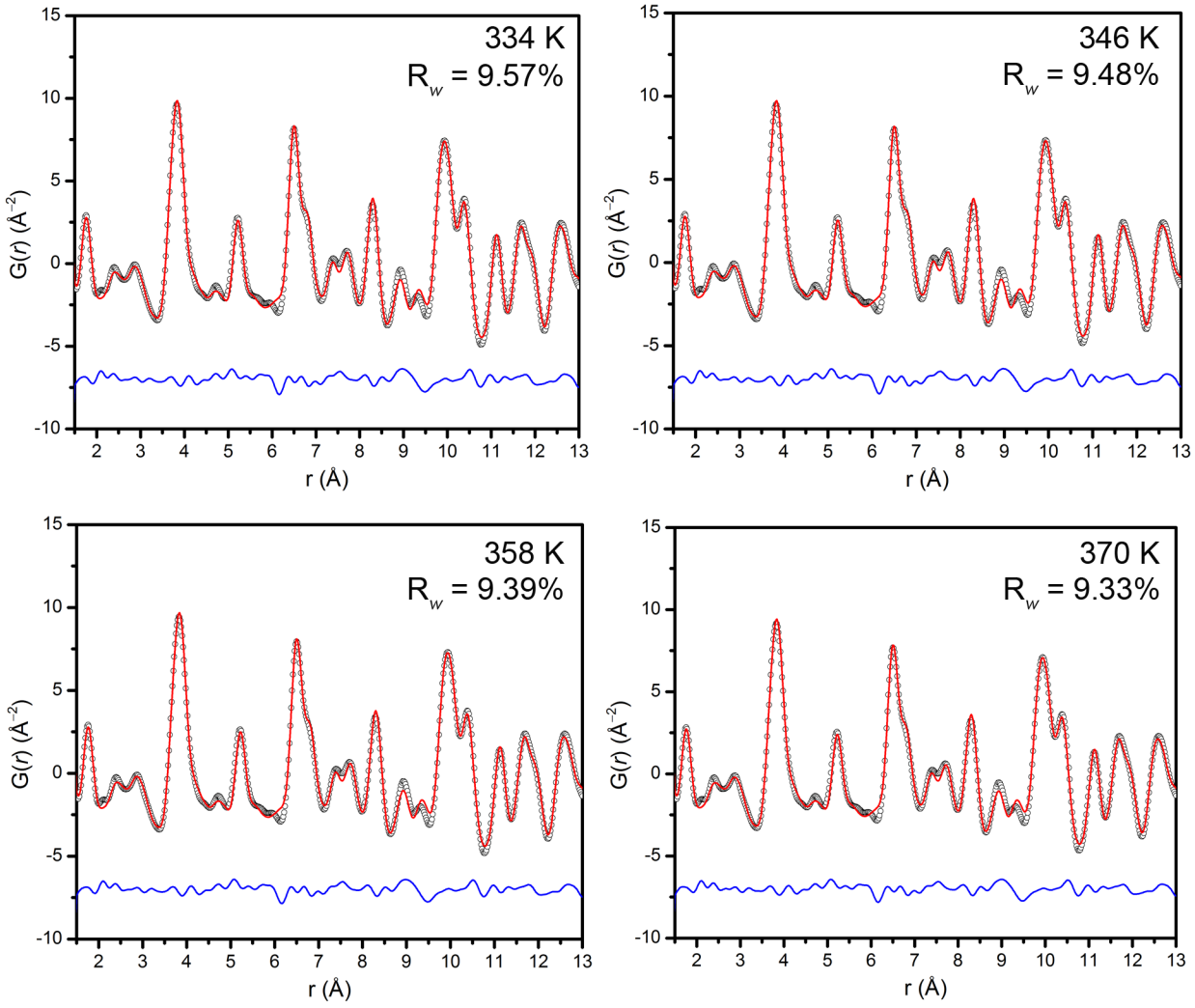

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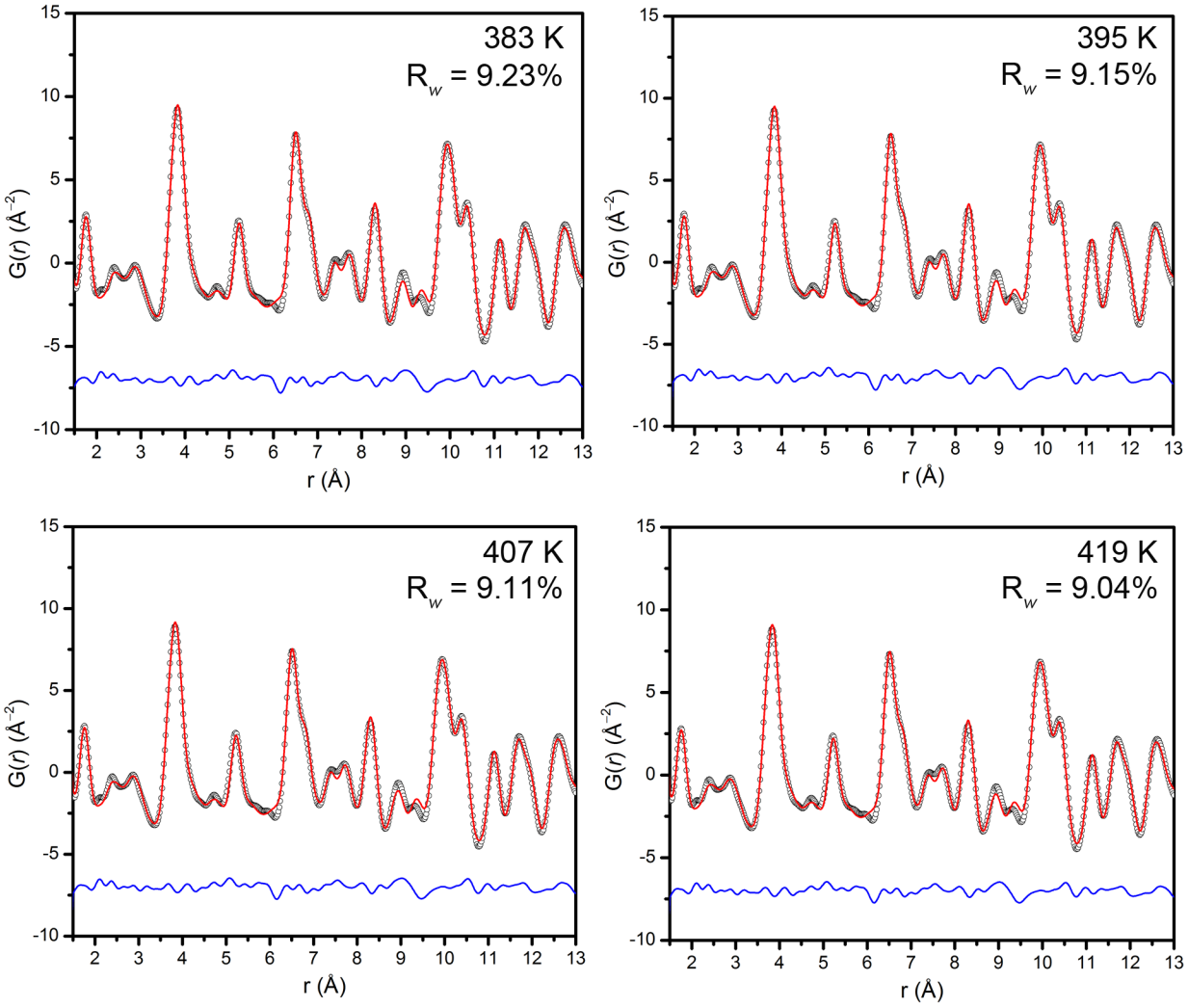

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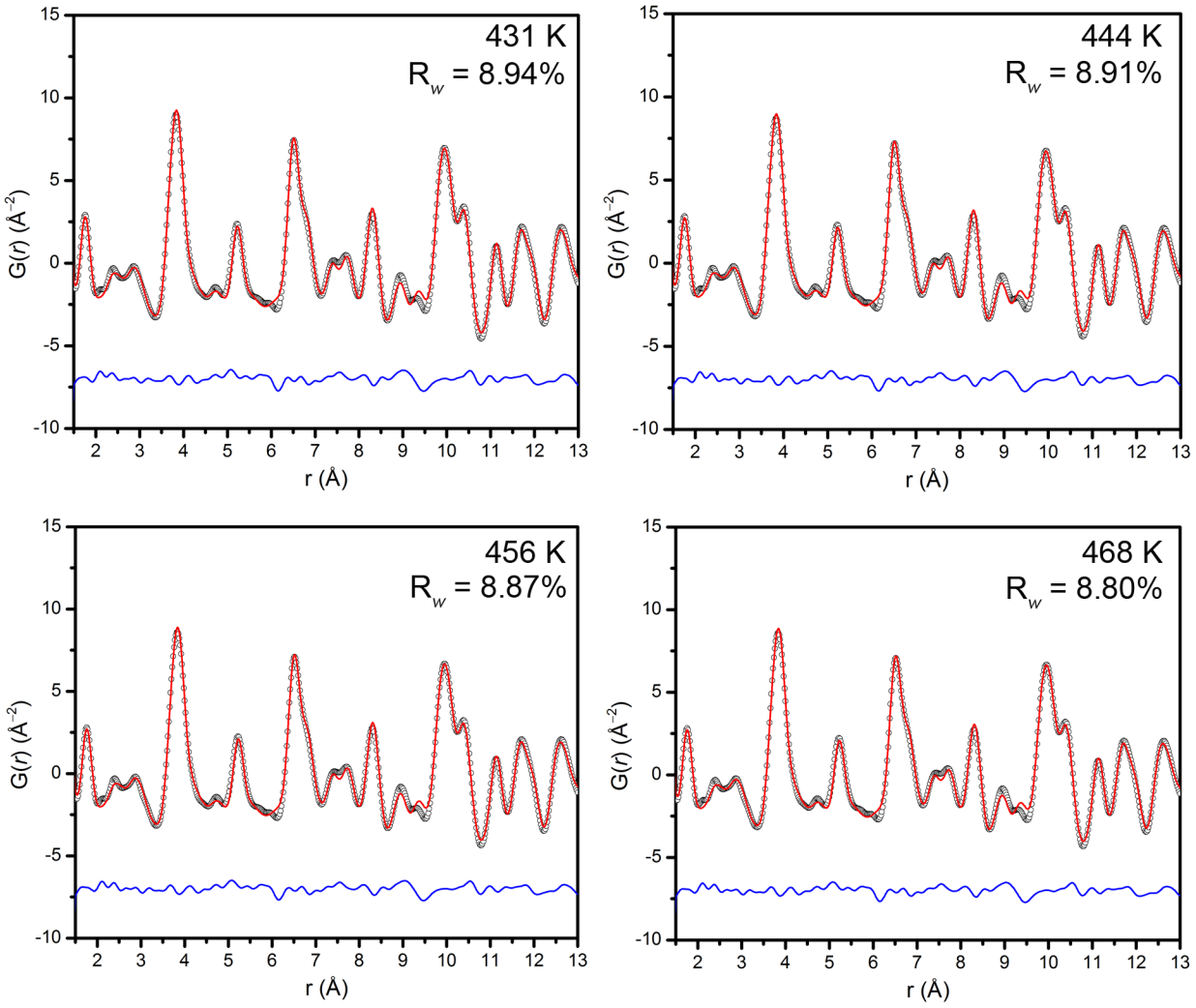

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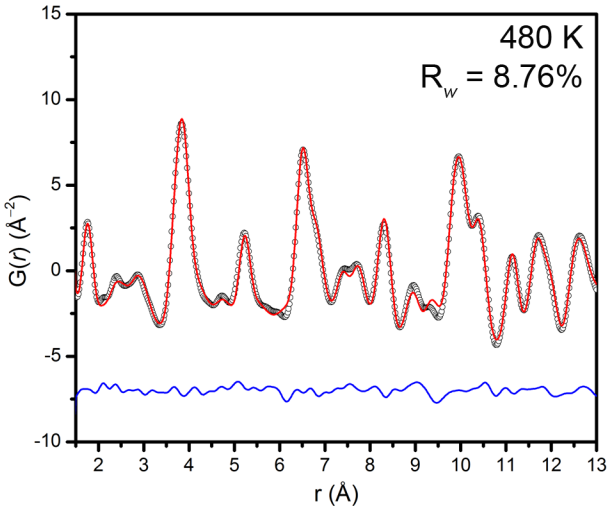

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Table S1 Structural Parameters of $CaMoO_4$ Nanocrystals From 90–480 K Extracted From Rietveld Analysis —*Continues on the following page*

	90 K	102 K	114 K	127 K	139 K
a (Å)	5.2181(4)	5.2185(4)	5.2188(4)	5.2192(4)	5.2197(4)
c (Å)	11.404(1)	11.406(1)	11.407(1)	11.408(1)	11.410(1)
V (Å^3)	310.53(7)	310.60(7)	310.68(7)	310.76(7)	310.86(7)
x_O	0.6470(7)	0.6470(7)	0.6470(7)	0.6469(7)	0.6468(7)
y_O	0.5124(7)	0.5125(7)	0.5125(7)	0.5126(7)	0.5126(7)
z_O	0.2090(4)	0.2090(4)	0.2090(4)	0.2090(4)	0.2090(4)
Ca: U^{11}, U^{33} (Å^2)[a]	0.3, 0.7	0.3, 0.7	0.4, 0.7	0.4, 0.7	0.4, 0.8
U_{eq} (Å^2)	0.4	0.4	0.5	0.5	0.3
Mo: U^{11}, U^{33} (Å^2)	0.2, 0.4	0.3, 0.4	0.3, 0.4	0.3, 0.5	0.3, 0.5
U_{eq} (Å^2)	0.3	0.3	0.3	0.4	0.4
O: U^{11}, U^{22}, U^{33} (Å^2)	0.6, 0.4, 1.5	0.7, 0.4, 1.5	0.7, 0.5, 1.5	0.7, 0.5, 1.6	0.7, 0.5, 1.6
U^{12}, U^{13}, U^{23} (Å^2)	−0.3, 0.3, −0.1	−0.3, 0.3, −0.1	−0.3, 0.3, −0.2	−0.3, 0.3, −0.1	−0.3, 0.3, −0.2
U_{eq} (Å^2)	0.8	0.9	0.9	0.9	0.9
Ca–O (1) (Å)	2.459(4)	2.459(4)	2.460(4)	2.460(4)	2.461(4)
Ca–O (2) (Å)	2.487(4)	2.487(4)	2.487(4)	2.488(4)	2.489(4)
V_{CaO_8} (Å^3)	26.88	26.89	26.90	26.92	26.93
Δ_{AO_8} (×10^3)	5.6	5.6	5.5	5.7	5.8
Mo–O (Å)	1.745(3)	1.745(3)	1.744(3)	1.744(3)	1.744(3)
V_{MoO_4} (Å^3)	2.71	2.71	2.71	2.71	2.71
Ca–O–Mo (1) (°)	120.4(2)	120.4(2)	120.4(2)	120.4(2)	120.4(2)
Ca–O–Mo (2) (°)	132.9(2)	133.0(2)	132.9(2)	133.0(2)	133.0(2)

[a] Atomic displacements parameters are given as $100\times U^{ij}$.

Table S1 Structural Parameters of $CaMoO_4$ Nanocrystals From 90–480 K Extracted From Rietveld Analysis —*Continues on the following page*

	151 K	163 K	175 K	188 K	200 K
a (Å)	5.2202(4)	5.2207(4)	5.2213(5)	5.2218(5)	5.2224(5)
c (Å)	11.411(1)	11.413(1)	11.415(1)	11.417(1)	11.419(1)
V (Å^3)	310.96(7)	311.07(7)	311.19(7)	311.30(7)	311.42(7)
x_O	0.6469(7)	0.6467(8)	0.6467(8)	0.6466(8)	0.6466(8)
y_O	0.5126(7)	0.5126(7)	0.5127(7)	0.5128(7)	0.5128(7)
z_O	0.2090(4)	0.2090(4)	0.2090(4)	0.2090(4)	0.2090(4)
Ca: U^{11}, U^{33} (Å^2)[a]	0.4, 0.8	0.4, 0.8	0.4, 0.8	0.4, 0.9	0.5, 0.9
U_{eq} (Å^2)	0.5	0.5	0.5	0.6	0.6
Mo: U^{11}, U^{33} (Å^2)	0.3, 0.5	0.3, 0.5	0.4, 0.6	0.4, 0.6	0.4, 0.6
U_{eq} (Å^2)	0.4	0.4	0.5	0.5	0.5
O: U^{11}, U^{22}, U^{33} (Å^2)	0.7, 0.5, 1.6	0.8, 0.5, 1.7	0.8, 0.5, 1.7	0.9, 0.5, 1.7	0.9, 0.6, 1.8
U^{12}, U^{13}, U^{23} (Å^2)	−0.3, 0.3, −0.2	−0.3, 0.3 , −0.1	−0.3, 0.3 , −0.1	−0.3, 0.3 , −0.1	−0.3, 0.3 , −0.1
U_{eq} (Å^2)	0.9	1.0	1.0	1.0	1.1
Ca–O (1) (Å)	2.461(4)	2.461(4)	2.462(4)	2.462(4)	2.463(4)
Ca–O (2) (Å)	2.489(4)	2.490(4)	2.491(4)	2.491(4)	2.492(4)
V_{CaO_8} (Å^3)	26.94	26.96	26.98	27.00	27.01
Δ_{AO_8} (×10^3)	5.7	5.9	5.9	5.9	5.8
Mo–O (Å)	1.744(3)	1.744(3)	1.744(3)	1.744(3)	1.744(3)
V_{MoO_4} (Å^3)	2.71	2.71	2.71	2.71	2.71
Ca–O–Mo (1) (°)	120.4(2)	120.3(2)	120.3(2)	120.3(2)	120.3(2)
Ca–O–Mo (2) (°)	133.0(2)	133.0(2)	133.0(2)	133.1(2)	133.1(2)

[a] Atomic displacements parameters are given as $100\times U^{ij}$.

Table S1 Structural Parameters of $CaMoO_4$ Nanocrystals From 90–480 K Extracted From Rietveld Analysis —*Continues on the following page*

	212 K	224 K	236 K	248 K	261 K
a (Å)	5.2230(5)	5.2236(5)	5.2242(5)	5.2248(5)	5.2254(5)
c (Å)	11.421(1)	11.423(1)	11.425(1)	11.427(2)	11.429(2)
V (Å^3)	311.56(8)	311.68(8)	311.81(8)	311.94(8)	312.06(8)
x_O	0.6465(8)	0.6465(8)	0.6463(8)	0.6463(8)	0.6462(8)
y_O	0.5129(7)	0.5129(7)	0.5130(7)	0.5131(7)	0.5131(7)
z_O	0.2090(4)	0.2090(4)	0.2090(4)	0.2089(4)	0.2089(4)
Ca: U^{11}, U^{33} (Å^2)[a]	0.5, 0.9	0.5, 1.0	0.5, 1.0	0.5, 1.0	0.5, 1.0
U_{eq} (Å^2)	0.6	0.7	0.7	0.7	0.7
Mo: U^{11}, U^{33} (Å^2)	0.4, 0.6	0.5, 0.6	0.5, 0.7	0.5, 0.7	0.5, 0.7
U_{eq} (Å^2)	0.5	0.5	0.6	0.6	0.6
O: U^{11}, U^{22}, U^{33} (Å^2)	0.9, 0.6, 1.8	0.9, 0.7, 1.8	1.0, 0.7, 1.8	1.0, 0.7, 1.9	1.0, 0.7, 1.9
U^{12}, U^{13}, U^{23} (Å^2)	−0.3, 0.3 , −0.1	−0.2, 0.3 , −0.1	−0.2, 0.3 , −0.1	−0.2, 0.3 , 0.0	−0.2, 0.3 , 0.0
U_{eq} (Å^2)	1.1	1.1	1.2	1.2	1.2
Ca–O (1) (Å)	2.463(4)	2.464(4)	2.464(4)	2.465(4)	2.465(4)
Ca–O (2) (Å)	2.493(4)	2.493(4)	2.494(5)	2.495(5)	2.496(5)
V_{CaO_8} (Å^3)	27.04	27.05	27.08	27.10	27.12
Δ_{AO_8} (×10^3)	6.0	6.0	6.1	6.0	6.1
Mo–O (Å)	1.743(3)	1.743(3)	1.743(4)	1.743(4)	1.742(4)
V_{MoO_4} (Å^3)	2.71	2.71	2.71	2.71	2.71
Ca–O–Mo (1) (°)	120.3(2)	120.3(2)	120.3(2)	120.3(2)	120.3(2)
Ca–O–Mo (2) (°)	133.1(2)	133.1(2)	133.1(2)	133.1(2)	133.2(2)

[a] Atomic displacements parameters are given as $100\times U^{ij}$.

Table S1 Structural Parameters of $CaMoO_4$ Nanocrystals From 90–480 K Extracted From Rietveld Analysis —*Continues on the following page*

	273 K	285 K	297 K	309 K	322 K
a (Å)	5.2259(5)	5.2265(5)	5.2270(5)	5.2278(5)	5.2284(5)
c (Å)	11.431(2)	11.433(2)	11.435(2)	11.437(2)	11.440(2)
V (Å^3)	312.18(8)	312.31(8)	312.42(8)	312.56(8)	312.73(8)
x_O	0.6462(8)	0.6461(8)	0.6461(8)	0.6460(8)	0.6459(8)
y_O	0.5132(7)	0.5132(7)	0.5133(7)	0.5133(7)	0.5134(7)
z_O	0.2089(4)	0.2089(4)	0.2089(4)	0.2089(4)	0.2089(4)
Ca: U^{11}, U^{33} (Å^2)[a]	0.6, 1.1	0.6, 1.1	0.6, 1.1	0.6, 1.2	0.6, 1.2
U_{eq} (Å^2)	0.8	0.8	0.8	0.8	0.8
Mo: U^{11}, U^{33} (Å^2)	0.5, 0.7	0.5, 0.8	0.6, 0.8	0.6, 0.8	0.6, 0.8
U_{eq} (Å^2)	0.6	0.6	0.7	0.7	0.8
O: U^{11}, U^{22}, U^{33} (Å^2)	1.0, 0.7, 1.9	1.1, 0.8, 2.0	1.1, 0.8, 2.0	1.2, 0.8, 2.0	1.2, 0.8, 2.1
U^{12}, U^{13}, U^{23} (Å^2)	−0.2, 0.3 , 0.0	−0.2, 0.3 , 0.0	−0.2, 0.3 , 0.0	−0.2, 0.3 , 0.0	−0.1, 0.3 , 0.1
U_{eq} (Å^2)	1.2	1.3	1.3	1.3	1.4
Ca–O (1) (Å)	2.466(4)	2.466(4)	2.466(4)	2.467(4)	2.468(4)
Ca–O (2) (Å)	2.496(5)	2.497(5)	2.497(5)	2.498(5)	2.499(5)
V_{CaO_8} (Å^3)	27.14	27.15	27.17	27.19	27.21
Δ_{AO_8} (×10^3)	6.1	6.1	6.2	6.2	6.3
Mo–O (Å)	1.742(4)	1.742(4)	1.742(4)	1.742(4)	1.742(4)
V_{MoO_4} (Å^3)	2.70	2.70	2.71	2.70	2.70
Ca–O–Mo (1) (°)	120.3(2)	120.3(3)	120.3(3)	120.3(3)	120.3(3)
Ca–O–Mo (2) (°)	133.2(2)	133.2(2)	133.2(2)	133.2(2)	133.3(2)

[a] Atomic displacements parameters are given as $100\times U^{ij}$.

Table S1 Structural Parameters of $CaMoO_4$ Nanocrystals From 90–480 K Extracted From Rietveld Analysis —*Continues on the following page*

	334 K	346 K	358 K	370 K	383 K
a (Å)	5.2290(5)	5.2297(5)	5.2303(5)	5.2309(5)	5.2314(5)
c (Å)	11.442(2)	11.445(2)	11.447(2)	11.450(2)	11.452(2)
V (Å^3)	312.86(8)	313.00(8)	313.14(9)	313.29(9)	313.41(9)
x_O	0.6459(8)	0.6459(8)	0.6458(9)	0.6457(9)	0.6456(9)
y_O	0.5135(7)	0.5136(7)	0.5138(7)	0.5139(8)	0.5142(8)
z_O	0.2089(4)	0.2088(4)	0.2088(4)	0.2088(5)	0.2088(5)
Ca: U^{11}, U^{33} (Å^2)[a]	0.7, 1.2	0.7, 1.3	0.7, 1.3	0.7, 1.4	0.8, 1.4
U_{eq} (Å^2)	0.9	0.9	0.9	0.9	1.0
Mo: U^{11}, U^{33} (Å^2)	0.6, 0.9	0.7, 0.9	0.7, 0.9	0.7, 0.9	0.7, 1.0
U_{eq} (Å^2)	0.7	0.8	0.8	0.8	0.8
O: U^{11}, U^{22}, U^{33} (Å^2)	1.3, 0.8, 2.1	1.3, 0.9, 2.2	1.4, 0.9, 2.2	1.4, 0.9, 2.2	1.4, 0.9, 2.3
U^{12}, U^{13}, U^{23} (Å^2)	–0.1, 0.3 , 0.1	–0.1, 0.3 , 0.1	–0.1, 0.3 , 0.1	0.0, 0.3 , 0.2	0.0, 0.3 , 0.2
U_{eq} (Å^2)	1.4	1.5	1.5	1.5	1.5
Ca–O (1) (Å)	2.468(4)	2.470(4)	2.470(5)	2.471(5)	2.472(5)
Ca–O (2) (Å)	2.500(5)	2.500(5)	2.501(5)	2.502(5)	2.504(5)
V_{AO_8} (Å^3)	27.24	27.27	27.30	27.33	27.36
Δ_{AO_8} ($\times 10^3$)	6.3	6.2	6.3	6.3	6.4
Mo–O (Å)	1.742(4)	1.741(4)	1.740(4)	1.740(4)	1.739(4)
V_{MoO_4} (Å^3)	2.70	2.70	2.70	2.69	2.69
Ca–O–Mo (1) (°)	120.3(3)	120.3(3)	120.3(3)	120.3(3)	120.3(3)
Ca–O–Mo (2) (°)	133.3(2)	133.3(3)	133.3(3)	133.3(3)	133.4(3)

[a] Atomic displacements parameters are given as $100\times U^{ij}$.

Table S1 Structural Parameters of $CaMoO_4$ Nanocrystals From 90–480 K Extracted From Rietveld Analysis —*Continues on the following page*

	395 K	407 K	419 K	431 K	444 K
a (Å)	5.2320(5)	5.2326(6)	5.2331(6)	5.2335(6)	5.2339(6)
c (Å)	11.454(2)	11.457(2)	11.459(2)	11.461(2)	11.463(2)
V (Å^3)	313.54(9)	313.68(9)	313.80(9)	313.92(9)	314.03(9)
x_O	0.6456(9)	0.6455(9)	0.6455(9)	0.6454(9)	0.6452(9)
y_O	0.5143(8)	0.5146(8)	0.5148(8)	0.5151(8)	0.5152(8)
z_O	0.2088(5)	0.2088(5)	0.2088(5)	0.2088(5)	0.2089(5)
Ca: U^{11}, U^{33} (Å^2)[a]	0.8, 1.4	0.8, 1.5	0.9, 1.5	0.9, 1.5	0.9, 1.6
U_{eq} (Å^2)	1.0	1.0	1.1	1.1	1.1
Mo: U^{11}, U^{33} (Å^2)	0.7, 1.0	0.8, 1.0	0.8, 1.0	0.8, 1.0	0.8, 1.1
U_{eq} (Å^2)	0.8	0.9	0.9	0.9	0.9
O: U^{11}, U^{22}, U^{33} (Å^2)	1.5, 0.9, 2.4	1.6, 1.0, 2.4	1.6, 1.0, 2.5	1.7, 1.0, 2.5	1.7, 1.0, 2.5
U^{12}, U^{13}, U^{23} (Å^2)	0.0, 0.3 , 0.2	0.0, 0.3 , 0.3	0.0, 0.3 , 0.3	0.0, 0.3 , 0.3	0.0, 0.3 , 0.3
U_{eq} (Å^2)	1.6	1.7	1.7	1.7	1.7
Ca–O (1) (Å)	2.473(5)	2.474(5)	2.475(5)	2.476(5)	2.476(5)
Ca–O (2) (Å)	2.505(5)	2.506(5)	2.507(5)	2.508(5)	2.510(5)
V_{AO_8} (Å^3)	27.39	27.43	27.46	27.50	27.53
Δ_{AO_8} ($\times 10^3$)	6.4	6.5	6.4	6.5	6.7
Mo–O (Å)	1.738(4)	1.738(4)	1.737(4)	1.736(4)	1.736(4)
V_{MoO_4} (Å^3)	2.69	2.69	2.68	2.68	2.68
Ca–O–Mo (1) (°)	120.3(3)	120.3(3)	120.3(3)	120.3(3)	120.2(3)
Ca–O–Mo (2) (°)	133.4(3)	133.4(3)	133.4(3)	133.4(3)	133.5(3)

[a] Atomic displacements parameters are given as $100 \times U^{ij}$.

Table S1 Structural Parameters of $CaMoO_4$ Nanocrystals From 90–480 K Extracted From Rietveld Analysis

	456 K	468 K	480 K
a (Å)	5.2343(6)	5.2347(6)	5.2350(6)
c (Å)	11.466(2)	11.468(2)	11.469(2)
V (Å^3)	314.1(1)	314.2(1)	314.3(1)
x_O	0.6451(9)	0.6451(9)	0.645(1)
y_O	0.5154(8)	0.5156(8)	0.5156(8)
z_O	0.2089(5)	0.2089(5)	0.2089(5)
Ca: U^{11}, U^{33} (Å^2)[a]	0.9, 1.6	0.9, 1.6	0.9, 1.7
U_{eq} (Å^2)	1.1	1.1	1.2
Mo: U^{11}, U^{33} (Å^2)	0.8, 1.1	0.9, 1.1	0.9, 1.1
U_{eq} (Å^2)	0.9	1.0	1.0
O: U^{11}, U^{22}, U^{33} (Å^2)	1.8, 1.0, 2.6	1.8, 1.0, 2.6	1.9, 1.0, 2.6
U^{12}, U^{13}, U^{23} (Å^2)	0.0, 0.2 , 0.3	0.0, 0.2 , 0.3	0.0, 0.2 , 0.4
U_{eq} (Å^2)	1.8	1.8	1.8
Ca–O (1) (Å)	2.477(5)	2.477(5)	2.478(5)
Ca–O (2) (Å)	2.511(5)	2.512(5)	2.513(5)
V_{AO_8} (Å^3)	27.56	27.58	27.60
Δ_{AO_8} ($\times 10^3$)	6.9	6.9	7.1
Mo–O (Å)	1.735(4)	1.734(4)	1.734(4)
V_{MoO_4} (Å^3)	2.67	2.67	2.67
Ca–O–Mo (1) (°)	120.2(3)	120.2(3)	120.2(3)
Ca–O–Mo (2) (°)	133.6(3)	133.6(3)	133.6(3)

[a] Atomic displacements parameters are given as $100 \times U^{ij}$.

Table S2 Structural Parameters of $CaMoO_4$ Nanocrystals From 90–480 K Extracted From PDF Analysis —*Continues on the following page*

	90 K	102 K	114 K	127 K	139 K
a (Å)	5.213	5.213	5.213	5.213	5.214
c (Å)	11.373	11.374	11.376	11.377	11.379
V (Å^3)	309.0	309.1	309.1	309.2	309.3
x_O	0.650	0.649	0.649	0.648	0.648
y_O	0.506	0.506	0.506	0.506	0.506
z_O	0.211	0.211	0.211	0.211	0.211
Ca: U^{11}, U^{33} (Å^2)[a]	0.6, 0.9	0.6, 0.9	0.6, 1.0	0.6, 1.0	0.6, 1.0
U_{eq} (Å^2)	0.7	0.7	0.7	0.7	0.7
Mo: U^{11}, U^{33} (Å^2)	0.4, 0.5	0.4, 0.5	0.4, 0.5	0.4, 0.5	0.4, 0.6
U_{eq} (Å^2)	0.4	0.4	0.5	0.5	0.5
O: U^{11}, U^{22}, U^{33} (Å^2)	1.0, 3.0, 1.5	1.1, 3.1, 1.6	1.3, 3.2, 1.6	1.4, 3.2, 1.6	1.5, 3.3, 1.6
U^{12}, U^{13}, U^{23} (Å^2)	−0.2, 0.1, 1.3	−0.2, 0.0, 1.4	−0.2, 0.0, 1.4	−0.2, −0.1, 1.5	−0.2, −0.1, 1.5
U_{eq} (Å^2)	1.9	1.9	2.0	2.1	2.1
Ca–O (1) (Å)	2.426	2.425	2.424	2.422	2.421
Ca–O (2) (Å)	2.460	2.463	2.466	2.470	2.472
V_{AO_8} (Å^3)	25.91	25.94	25.97	26.01	26.03
Δ_{AO_8} ($\times 10^3$)	7.0	7.7	8.7	9.8	10.5
Mo–O (Å)	1.783	1.782	1.781	1.781	1.780
V_{MoO_4} (Å^3)	2.89	2.89	2.89	2.89	2.89
Ca–O–Mo (1) (°)	119.8	119.7	119.5	119.4	119.3
Ca–O–Mo (2) (°)	132.2	132.3	132.5	132.7	132.8

[a] Atomic displacements parameters are given as $100 \times U^{ij}$.

Table S2 Structural Parameters of $CaMoO_4$ Nanocrystals From 90–480 K Extracted From PDF Analysis —*Continues on the following page*

	151 K	163 K	175 K	188 K	200 K
a (Å)	5.214	5.214	5.214	5.215	5.216
c (Å)	11.381	11.384	11.386	11.388	11.390
V (Å^3)	309.4	309.5	309.6	309.7	309.8
x_O	0.647	0.644	0.644	0.643	0.643
y_O	0.507	0.508	0.508	0.508	0.508
z_O	0.211	0.213	0.213	0.213	0.213
Ca: U^{11}, U^{33} (Å^2)[a]	0.6, 1.0	0.6, 1.1	0.7, 1.1	0.7, 1.1	0.7, 1.2
U_{eq} (Å^2)	0.8	0.8	0.8	0.8	0.8
Mo: U^{11}, U^{33} (Å^2)	0.4, 0.6	0.5, 0.6	0.5, 0.6	0.5, 0.7	0.5, 0.7
U_{eq} (Å^2)	0.5	0.5	0.5	0.5	0.6
O: U^{11}, U^{22}, U^{33} (Å^2)	1.7, 3.3, 1.7	2.4, 3.2, 1.7	2.5, 3.3, 1.7	2.7, 3.4, 1.7	2.8, 3.4, 1.7
U^{12}, U^{13}, U^{23} (Å^2)	−0.2, −0.2, 1.5	−0.1, −0.4, 1.6	−0.1, −0.4, 1.6	−0.1, −0.5, 1.7	0.0, −0.5, 1.7
U_{eq} (Å^2)	2.2	2.4	2.5	2.6	2.6
Ca–O (1) (Å)	2.419	2.407	2.405	2.404	2.403
Ca–O (2) (Å)	2.477	2.496	2.499	2.503	2.505
V_{AO_8} (Å^3)	26.08	26.20	26.23	26.27	26.30
Δ_{AO_8} ($\times 10^3$)	11.9	18.3	19.2	20.3	20.8
Mo–O (Å)	1.779	1.777	1.777	1.776	1.776
V_{MoO_4} (Å^3)	2.88	2.88	2.88	2.87	2.87
Ca–O–Mo (1) (°)	119.1	118.3	118.2	118.0	118.0
Ca–O–Mo (2) (°)	133.0	134.0	134.2	134.4	134.5

[a] Atomic displacements parameters are given as $100 \times U^{ij}$.

Table S2 Structural Parameters of $CaMoO_4$ Nanocrystals From 90–480 K Extracted From PDF Analysis —*Continues on the following page*

	212 K	224 K	236 K	248 K	261 K
a (Å)	5.216	5.217	5.217	5.218	5.219
c (Å)	11.390	11.393	11.395	11.397	11.399
V (Å^3)	309.8	310.1	310.2	310.3	310.4
x_O	0.642	0.642	0.642	0.642	0.641
y_O	0.508	0.508	0.508	0.508	0.508
z_O	0.213	0.213	0.213	0.213	0.213
Ca: U^{11}, U^{33} (Å^2)[a]	0.7, 1.2	0.7, 1.2	0.8, 1.3	0.8, 1.3	0.8, 1.3
U_{eq} (Å^2)	0.9	0.9	0.9	0.9	1.0
Mo: U^{11}, U^{33} (Å^2)	0.5, 0.7	0.5, 0.7	0.5, 0.8	0.6, 0.8	0.6, 0.8
U_{eq} (Å^2)	0.6	0.6	0.6	0.6	0.6
O: U^{11}, U^{22}, U^{33} (Å^2)	2.9, 3.5, 1.8	3.0, 3.6, 1.8	3.1, 3.6, 1.8	3.2, 3.7, 1.9	3.2, 3.7, 1.9
U^{12}, U^{13}, U^{23} (Å^2)	0.0, −0.5, 1.7	0.0, −0.5, 1.8	0.0, −0.5, 1.8	0.0, −0.5, 1.8	0.0, −0.6, 1.8
U_{eq} (Å^2)	2.7	2.8	2.8	2.9	3.0
Ca–O (1) (Å)	2.402	2.401	2.401	2.401	2.401
Ca–O (2) (Å)	2.509	2.511	2.513	2.514	2.516
V_{AO_8} (Å^3)	26.34	26.37	26.39	26.42	26.44
Δ_{AO_8} ($\times 10^3$)	21.8	22.3	22.8	23.2	23.4
Mo–O (Å)	1.775	1.775	1.774	1.774	1.774
V_{MoO_4} (Å^3)	2.87	2.87	2.87	2.86	2.86
Ca–O–Mo (1) (°)	117.8	117.8	117.7	117.7	117.7
Ca–O–Mo (2) (°)	134.7	134.8	134.8	134.9	135.0

[a] Atomic displacements parameters are given as $100 \times U^{ij}$.

Table S2 Structural Parameters of $CaMoO_4$ Nanocrystals From 90–480 K Extracted From PDF Analysis —*Continues on the following page*

	273 K	285 K	297 K	309 K	322 K
a (Å)	5.219	5.220	5.221	5.221	5.222
c (Å)	11.401	11.403	11.404	11.406	11.409
V (Å^3)	310.6	310.7	310.8	311.0	311.1
x_O	0.641	0.641	0.641	0.641	0.641
y_O	0.508	0.508	0.508	0.508	0.508
z_O	0.213	0.213	0.213	0.213	0.213
Ca: U^{11}, U^{33} (Å^2)[a]	0.8, 1.3	0.8, 1.4	0.9, 1.4	0.9, 1.4	0.9, 1.5
U_{eq} (Å^2)	1.0	1.0	1.0	1.1	1.1
Mo: U^{11}, U^{33} (Å^2)	0.6, 0.8	0.6, 0.8	0.6, 0.9	0.6, 0.9	0.6, 0.9
U_{eq} (Å^2)	0.7	0.7	0.7	0.7	0.7
O: U^{11}, U^{22}, U^{33} (Å^2)	3.3, 3.7, 2.0	3.4, 3.8, 2.0	3.4, 3.8, 2.0	3.5, 3.8, 2.1	3.6, 3.9, 2.2
U^{12}, U^{13}, U^{23} (Å^2)	0.0, −0.6, 1.8	0.0, −0.6, 1.9	0.0, −0.6, 1.9	0.1, −0.6, 1.9	0.1, −0.7, 1.9
U_{eq} (Å^2)	3.0	3.0	3.1	3.1	3.2
Ca–O (1) (Å)	2.401	2.401	2.401	2.401	2.402
Ca–O (2) (Å)	2.516	2.517	2.518	2.519	2.520
V_{AO_8} (Å^3)	26.46	26.48	26.50	26.52	26.55
Δ_{AO_8} ($\times 10^3$)	23.4	23.7	23.8	24.0	23.9
Mo–O (Å)	1.774	1.773	1.773	1.773	1.773
V_{MoO_4} (Å^3)	2.86	2.86	2.86	2.86	2.86
Ca–O–Mo (1) (°)	117.7	117.6	117.6	117.6	117.6
Ca–O–Mo (2) (°)	135.0	135.1	135.1	135.1	135.2

[a] Atomic displacements parameters are given as $100 \times U^{ij}$.

Table S2 Structural Parameters of $CaMoO_4$ Nanocrystals From 90–480 K Extracted From PDF Analysis —*Continues on the following page*

	334 K	346 K	358 K	370 K	383 K
a (Å)	5.223	5.224	5.224	5.225	5.226
c (Å)	11.411	11.413	11.415	11.418	11.420
V (Å^3)	311.3	311.4	311.6	311.7	311.8
x_O	0.640	0.640	0.640	0.640	0.640
y_O	0.508	0.508	0.508	0.508	0.508
z_O	0.213	0.213	0.213	0.213	0.213
Ca: U^{11}, U^{33} (Å^2)[a]	1.0, 1.5	1.0, 1.5	1.0, 1.5	1.0, 1.6	1.1, 1.6
U_{eq} (Å^2)	1.1	1.2	1.2	1.2	1.3
Mo: U^{11}, U^{33} (Å^2)	0.7, 0.9	0.7, 1.0	0.7, 1.0	0.7, 1.0	0.7, 1.0
U_{eq} (Å^2)	0.8	0.8	0.8	0.8	0.8
O: U^{11}, U^{22}, U^{33} (Å^2)	3.6, 3.9, 2.2	3.7, 4.0, 2.3	3.7, 4.0, 2.4	3.8, 4.0, 2.4	3.9, 4.1, 2.5
U^{12}, U^{13}, U^{23} (Å^2)	0.1, –0.7, 1.9	0.1, –0.7, 2.0	0.1, –0.8, 1.9	0.1, –0.8, 2.0	0.1, –0.8, 2.0
U_{eq} (Å^2)	3.3	3.3	3.4	3.4	3.5
Ca–O (1) (Å)	2.403	2.403	2.405	2.405	2.405
Ca–O (2) (Å)	2.521	2.521	2.521	2.522	2.523
V_{AO_8} (Å^3)	26.57	26.59	26.61	26.63	26.65
Δ_{AO_8} ($\times 10^3$)	23.9	24.0	23.7	23.7	23.8
Mo–O (Å)	1.772	1.772	1.772	1.772	1.772
V_{MoO_4} (Å^3)	2.86	2.86	2.85	2.85	2.85
Ca–O–Mo (1) (°)	117.6	117.6	117.7	117.7	117.7
Ca–O–Mo (2) (°)	135.2	135.2	135.2	135.2	135.3

[a] Atomic displacements parameters are given as $100 \times U^{ij}$.

Table S2 Structural Parameters of $CaMoO_4$ Nanocrystals From 90–480 K Extracted From PDF Analysis —*Continues on the following page*

	395 K	407 K	419 K	431 K	444 K
a (Å)	5.226	5.227	5.228	5.228	5.229
c (Å)	11.422	11.424	11.426	11.429	11.431
V (Å^3)	312.0	312.1	312.3	312.4	312.5
x_O	0.640	0.640	0.640	0.640	0.640
y_O	0.508	0.508	0.508	0.508	0.508
z_O	0.213	0.213	0.213	0.213	0.213
Ca: U^{11}, U^{33} (Å^2)[a]	1.1, 1.6	1.1, 1.6	1.2, 1.7	1.2, 1.7	1.2, 1.7
U_{eq} (Å^2)	1.3	1.3	1.3	1.4	1.4
Mo: U^{11}, U^{33} (Å^2)	0.7, 1.1	0.8, 1.1	0.8, 1.1	0.8, 1.1	0.8, 1.2
U_{eq} (Å^2)	0.9	0.9	0.9	0.9	0.9
O: U^{11}, U^{22}, U^{33} (Å^2)	3.9, 4.1, 2.6	4.0, 4.0, 2.6	4.0, 4.1, 2.7	4.1, 4.1, 2.7	4.1, 4.1, 2.8
U^{12}, U^{13}, U^{23} (Å^2)	0.1, −0.8, 2.0	0.2, −0.9, 2.0	0.2, −0.9, 2.0	0.2, −0.9, 2.0	0.2, −0.9, 2.0
U_{eq} (Å^2)	3.5	3.5	3.6	3.6	3.7
Ca–O (1) (Å)	2.406	2.407	2.408	2.408	2.408
Ca–O (2) (Å)	2.523	2.523	2.524	2.524	2.525
V_{AO_8} (Å^3)	26.67	26.68	26.70	26.72	26.74
Δ_{AO_8} (×10^3)	23.6	23.7	23.5	23.5	23.7
Mo–O (Å)	1.771	1.771	1.771	1.771	1.771
V_{MoO_4} (Å^3)	2.85	2.85	2.85	2.85	2.85
Ca–O–Mo (1) (°)	117.7	117.7	117.7	117.7	117.7
Ca–O–Mo (2) (°)	135.2	135.3	135.3	135.3	135.3

[a] Atomic displacements parameters are given as $100\times U^{ij}$.

Table S2 Structural Parameters of $CaMoO_4$ Nanocrystals From 90–480 K Extracted From PDF Analysis

	456 K	468 K	480 K
a (Å)	5.229	5.230	5.230
c (Å)	11.433	11.435	11.436
V (Å^3)	312.6	312.8	312.9
x_O	0.640	0.640	0.640
y_O	0.508	0.508	0.508
z_O	0.213	0.213	0.213
Ca: U^{11}, U^{33} (Å^2)[a]	1.3, 1.7	1.3, 1.8	1.3, 1.8
U_{eq} (Å^2)	1.4	1.5	1.5
Mo: U^{11}, U^{33} (Å^2)	0.8, 1.2	0.8, 1.2	0.8, 1.2
U_{eq} (Å^2)	0.9	1.0	1.0
O: U^{11}, U^{22}, U^{33} (Å^2)	4.2, 4.1, 2.8	4.2, 4.1, 2.9	4.2, 4.1, 2.9
U^{12}, U^{13}, U^{23} (Å^2)	0.2, −1.0, 2.0	0.2, −1.0, 2.0	0.3, −1.0, 2.0
U_{eq} (Å^2)	3.7	3.7	3.8
Ca–O (1) (Å)	2.409	2.409	2.409
Ca–O (2) (Å)	2.525	2.527	2.527
V_{AO_8} (Å^3)	26.76	26.78	26.79
Δ_{AO_8} ($\times 10^3$)	23.5	23.9	23.8
Mo–O (Å)	1.771	1.771	1.770
V_{MoO_4} (Å^3)	2.85	2.85	2.85
Ca–O–Mo (1) (°)	117.7	117.7	117.7
Ca–O–Mo (2) (°)	135.3	135.4	135.4

[a] Atomic displacements parameters are given as $100 \times U^{ij}$.

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