Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Topotactic redox cycling in $SrFeO_{2.5+\delta}$ explored by 3D electron diffraction in different gas atmospheres

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S1. Study of the pristine $SrFeO_{2.5}$ sample

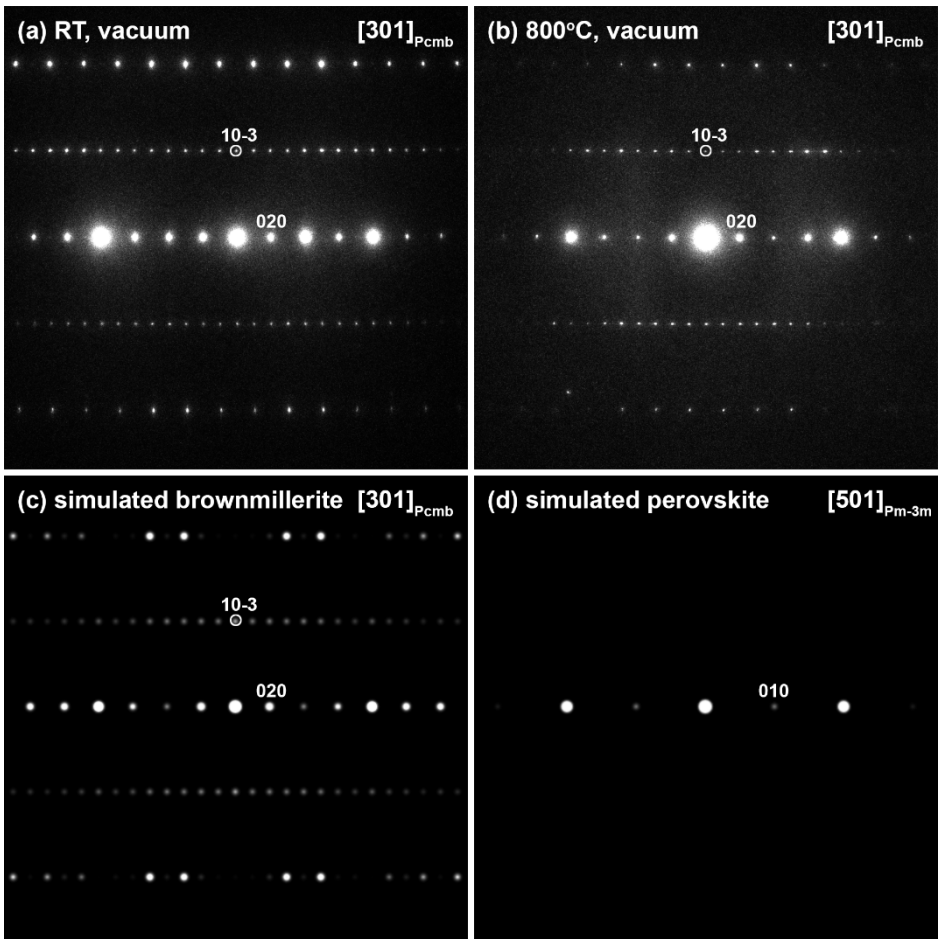

Figure S1. $[301]_{Pcmb}$ ED patterns of pristine $SrFeO_{2.5}$ at RT (a) and heated to 800°C in vacuum (b). All brownmillerite reflections corresponding to the *Pcmb* structure remained unchanged upon heating. Simulated ED patterns of brownmillerite *Pcmb* (c) and the equivalent zone for perovskite *Pm*-3*m* (d) for comparison.

S2. Relation between $SrFeO_x$ structures

The structural parameters of the $SrFeO_x$ phases (brownmillerite *Pcmb* and *Imma* for x = 2.5, *Cmmm* for x = 2.75, *I*4/*mmm* for x = 2.875 and perovskite (*p*) *Pm*-3*m* for x = 3-d) are listed in Table S1. The geometrical relation between different $SrFeO_x$ phases is described by the matrices ***P*** and ***Q*** (listed in Table S2) with the following equations:

$$\begin{pmatrix} u \\ v \\ w \end{pmatrix} = \boldsymbol{Q} \begin{pmatrix} u \\ v \\ w \end{pmatrix}_p$$

$(a, b, c) = (a, b, c)_p\boldsymbol{P}$

Table S1. The structural parameters of the $SrFeO_x$ phases.

Phase	**$SrFeO_{2.5}$**		**$SrFeO_{2.75}$**	**$SrFeO_{2.875}$**	**$SrFeO_3$**
Space group	*Pcmb*[1]	*Imma*[2]	*Cmmm*[2]	*I4/mmm*[2]	*Pm*-3*m*[2]
Relation to perovskite	$a_p\sqrt{2} \times 4a_p \times 2a_p\sqrt{2}$	$a_p\sqrt{2} \times 4a_p \times a_p\sqrt{2}$	$2a_p\sqrt{2} \times 2a_p \times a_p\sqrt{2}$	$2a_p\sqrt{2} \times 2a_p\sqrt{2} \times 2a_p$	$a_p \times a_p \times a_p$
Cell parameters	a = 5.53 Å b = 15.58 Å c = 11.35 Å	a = 5.53 Å b = 15.58 Å c = 5.53 Å	a = 10.974 Å b = 7.702 Å c = 5.473 Å	a = 10.929 Å c = 7.698 Å	a_p = 3.851 Å

Table S2. Transformation matrices from perovskite structure $SrFeO_3$ to other $SrFeO_x$ structures.

Transformation	***P***	***Q***
$SrFeO_3 \rightarrow SrFeO_{2.5}$ (*Imma*)	$\begin{pmatrix} 1 & 0 & 1 \\ 0 & 4 & 0 \\ 1 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1/2 & 0 & 1/2 \\ 0 & 1/4 & 0 \\ 1/2 & 0 & -1/2 \end{pmatrix}$
$SrFeO_3 \rightarrow SrFeO_{2.5}$ (*Pcmb*)	$\begin{pmatrix} 1 & 0 & 2 \\ 0 & 4 & 0 \\ 1 & 0 & -2 \end{pmatrix}$	$\begin{pmatrix} 1/2 & 0 & 1/2 \\ 0 & 1/4 & 0 \\ 1/4 & 0 & -1/4 \end{pmatrix}$
$SrFeO_3 \rightarrow SrFeO_{2.75}$ (*Cmmm*)	$\begin{pmatrix} 2 & 0 & 1 \\ 0 & 2 & 0 \\ -2 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1/4 & 0 & -1/4 \\ 0 & 1/2 & 0 \\ 1/2 & 0 & 1/2 \end{pmatrix}$
$SrFeO_3 \rightarrow SrFeO_{2.875}$ (*I4/mmm*)	$\begin{pmatrix} 2 & 2 & 0 \\ -2 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}$	$\begin{pmatrix} 1/4 & -1/4 & 0 \\ 1/4 & 1/4 & 0 \\ 0 & 0 & 1/2 \end{pmatrix}$

Figures S2-S6 represent simulated patterns for different $SrFeO_x$ structures. On the patterns the parent perovskite unit cell is outlined in green for $<100>_p$ orientations, red for $<110>_p$ orientations, and white for <301> orientations (subscript "p" stands for the perovskite basic cell).

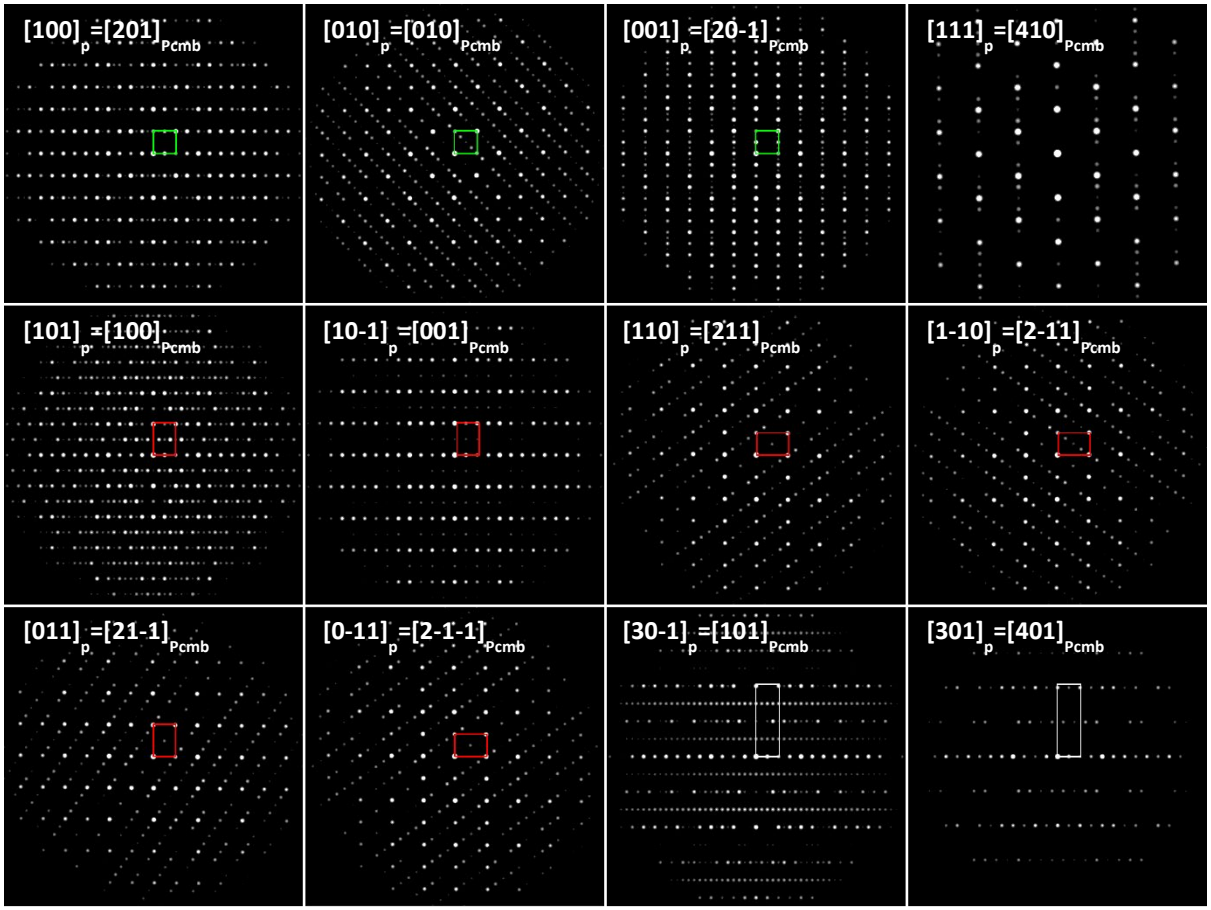

Figure S2. Simulated ED patterns of *Pcmb* brownmillerite $SrFeO_{2.5}$.[1]

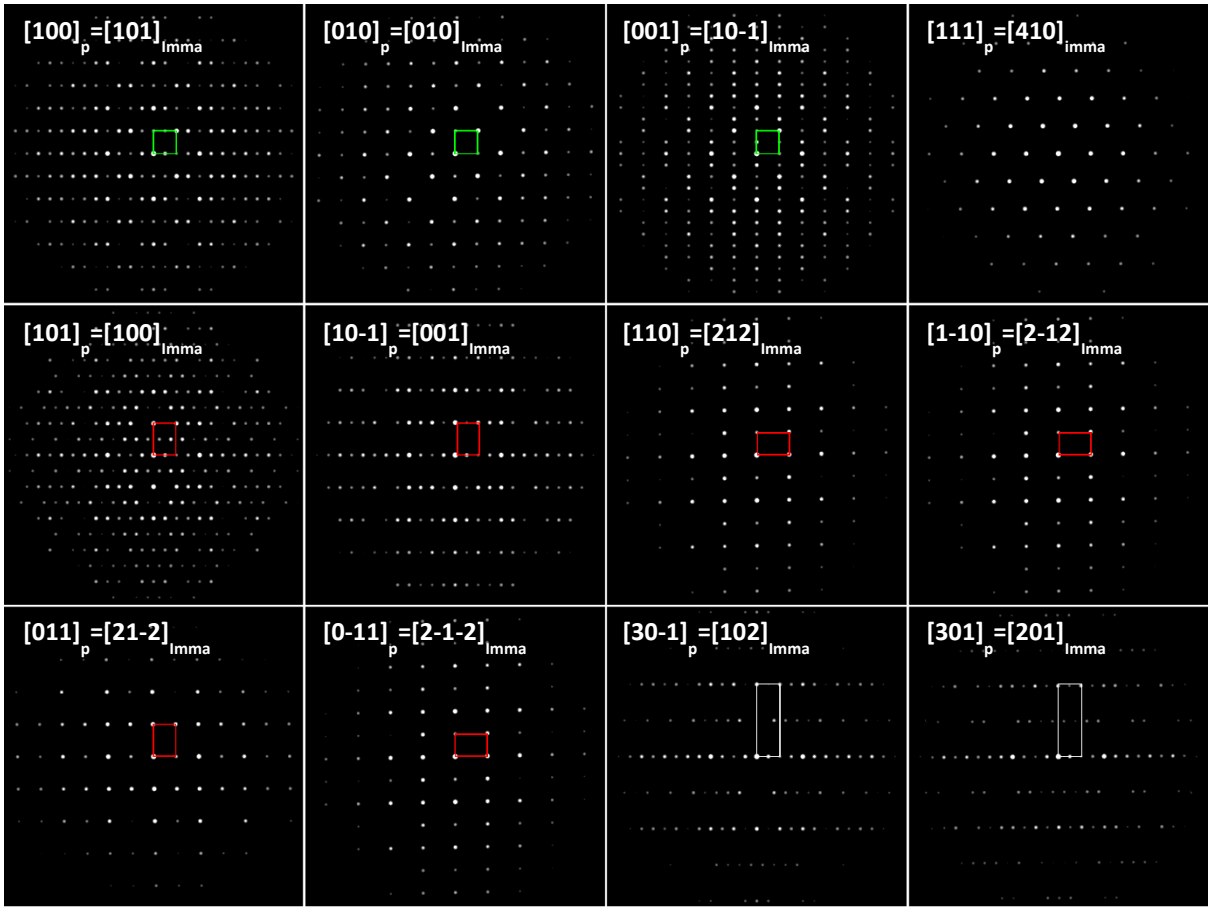

Figure S3. Simulated ED patterns of *Imma* brownmillerite $SrFeO_{2.5}$.[2]

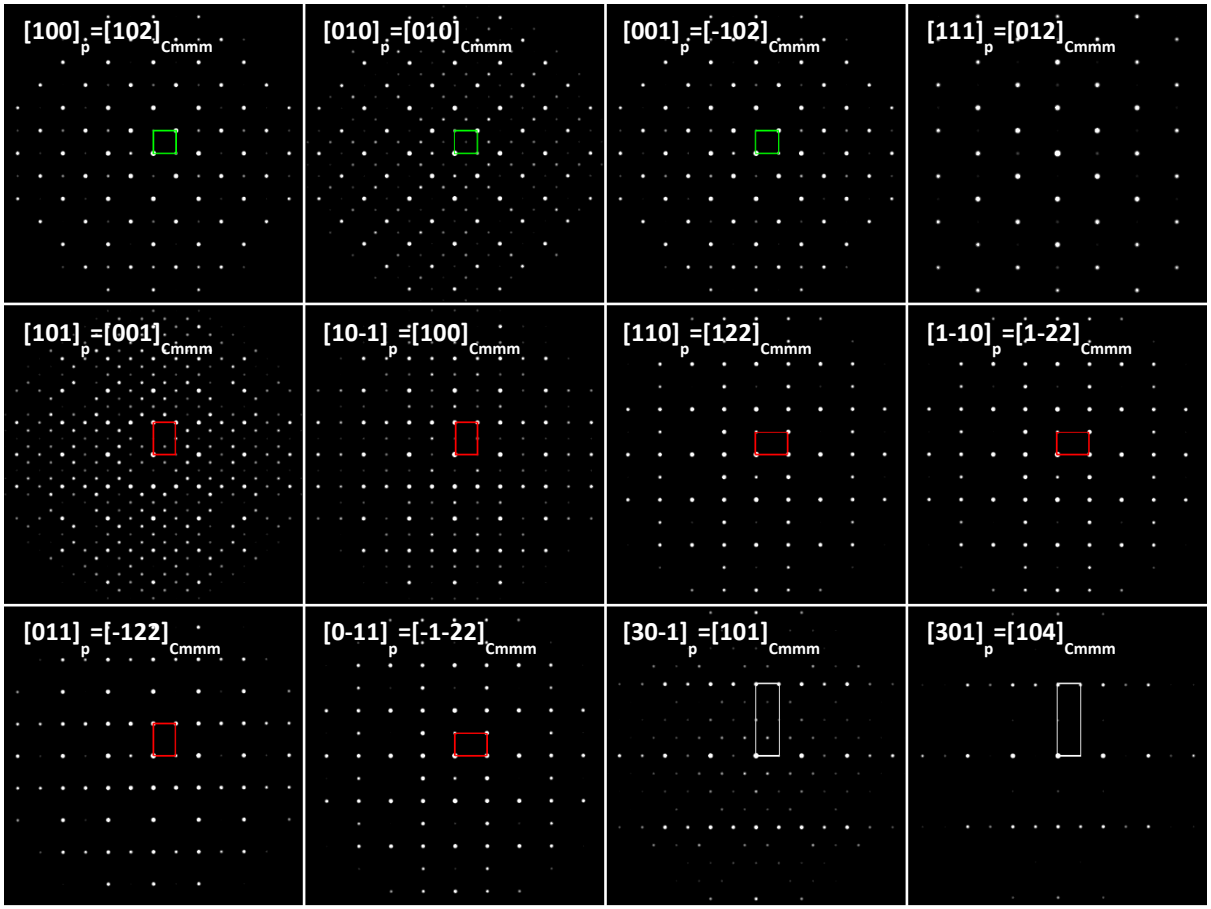

Figure S4. Simulated ED patterns of *Cmmm* phase $SrFeO_{2.75}$.[2]

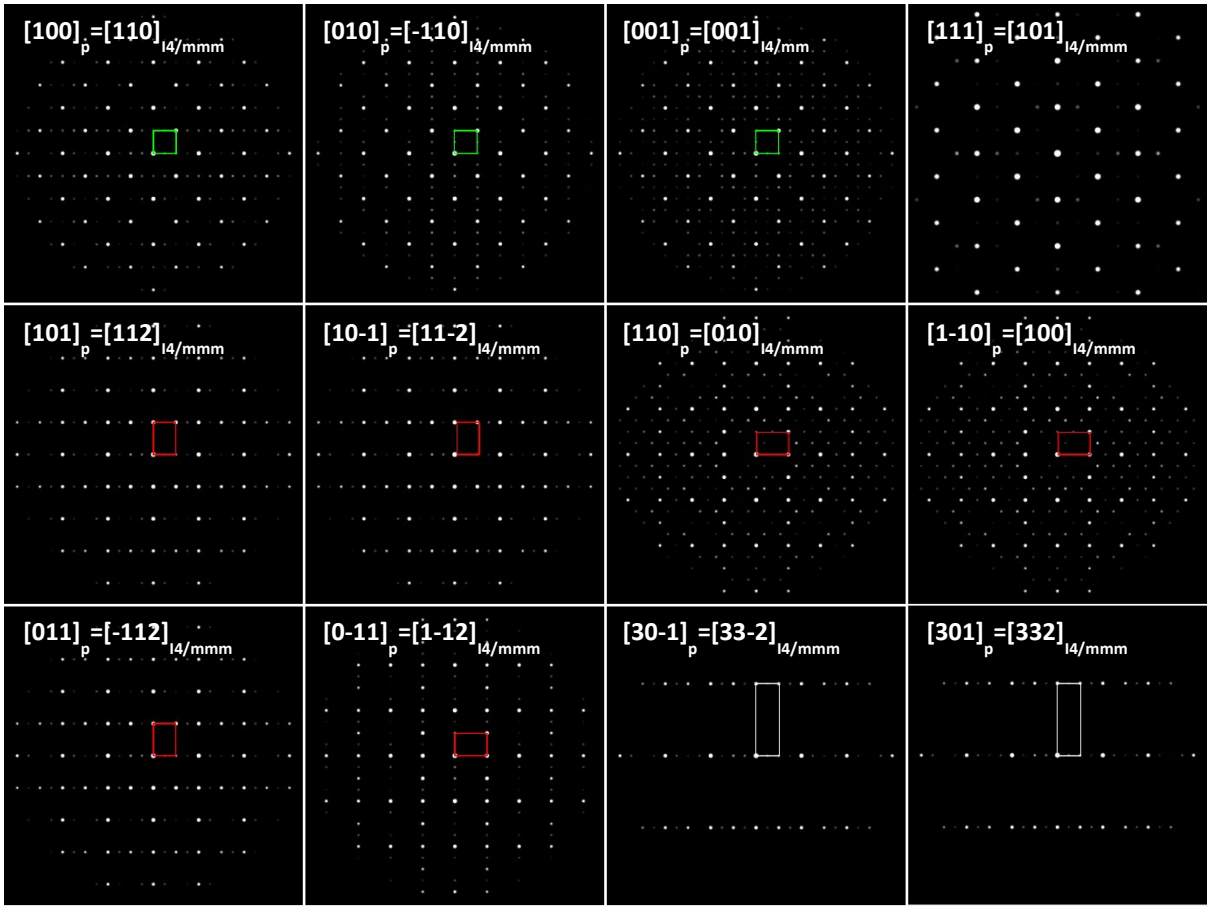

Figure S5. Simulated ED patterns of *I*4/*mmm* phase $SrFeO_{2.875}$.[2]

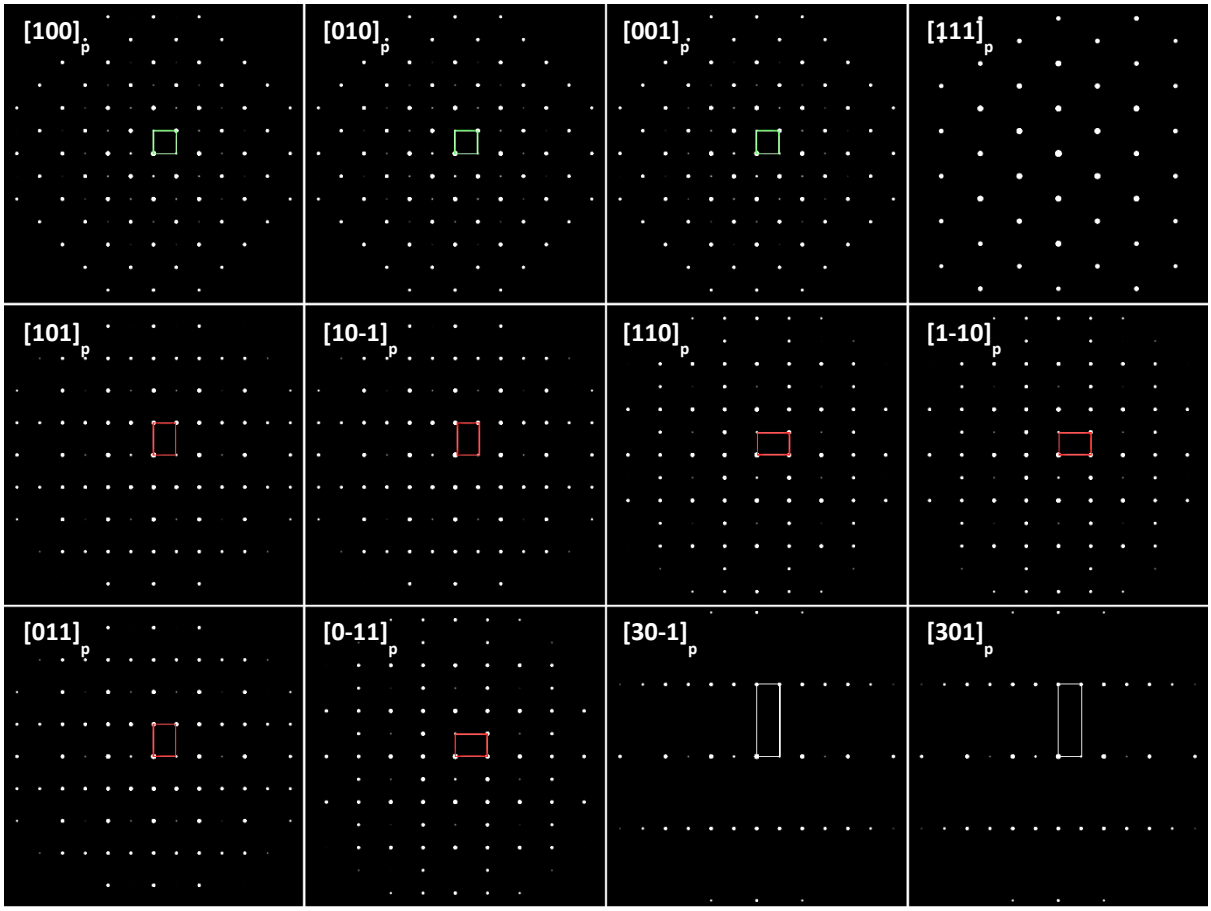

Figure S6. Simulated ED patterns of *Pm*-3*m* perovskite $SrFeO_3$.[2]

S3. Details and results on the *in situ* experiments

We performed a number of *in situ* experiments in different conditions (the varied parameters were temperature, heating rate, oxygen content) and analyzed crystals of different size and morphology. Here we show the results for two representative experiments.

Crystal 1 (Cr1, Figure S7) with a size of about 200 nm was heated with a ramping rate of 5°/minute up to 300°C in 33% O_2 (Figure S8), then to 350°C (Figure S9) and 400°C (Figure S10). It was kept overnight at these conditions (Figure S11). After the night, the oxygen concentration was increased to 100% O_2 (Figure S12) and kept at this value till the end of the experiment. The sample was heated to 600°C and cooled down to RT to perform a second cycle: the crystal was heated first to 200°C (Figure S13), then to 400°C (Figure S14 and Figure S15) and quenched to RT (Figure S16). At different stages of the experiment, 3D ED datasets were acquired (Figure S17).

Crystal 2 (Cr2, Figure S18) with a size of about 200 nm was heated with a ramping rate of 15°/minute up to 300°C in 10% O_2 where it directly transformed into perovskite structure (Figure S19) and remained the same at 500°C in 100% O_2 (Figure S20). We performed its reduction in 10% H_2 flow at 700°C (Figure S21).

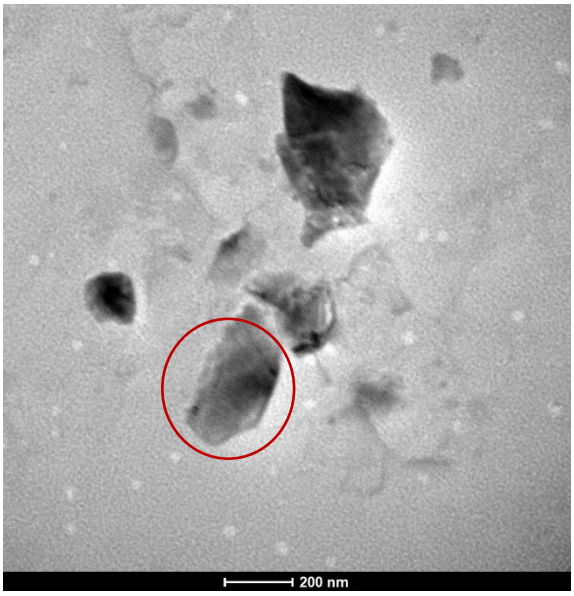

Figure S7. Overview TEM image of the small crystal Cr1. Red circle corresponds approximately to the position and size of the used selected area aperture.

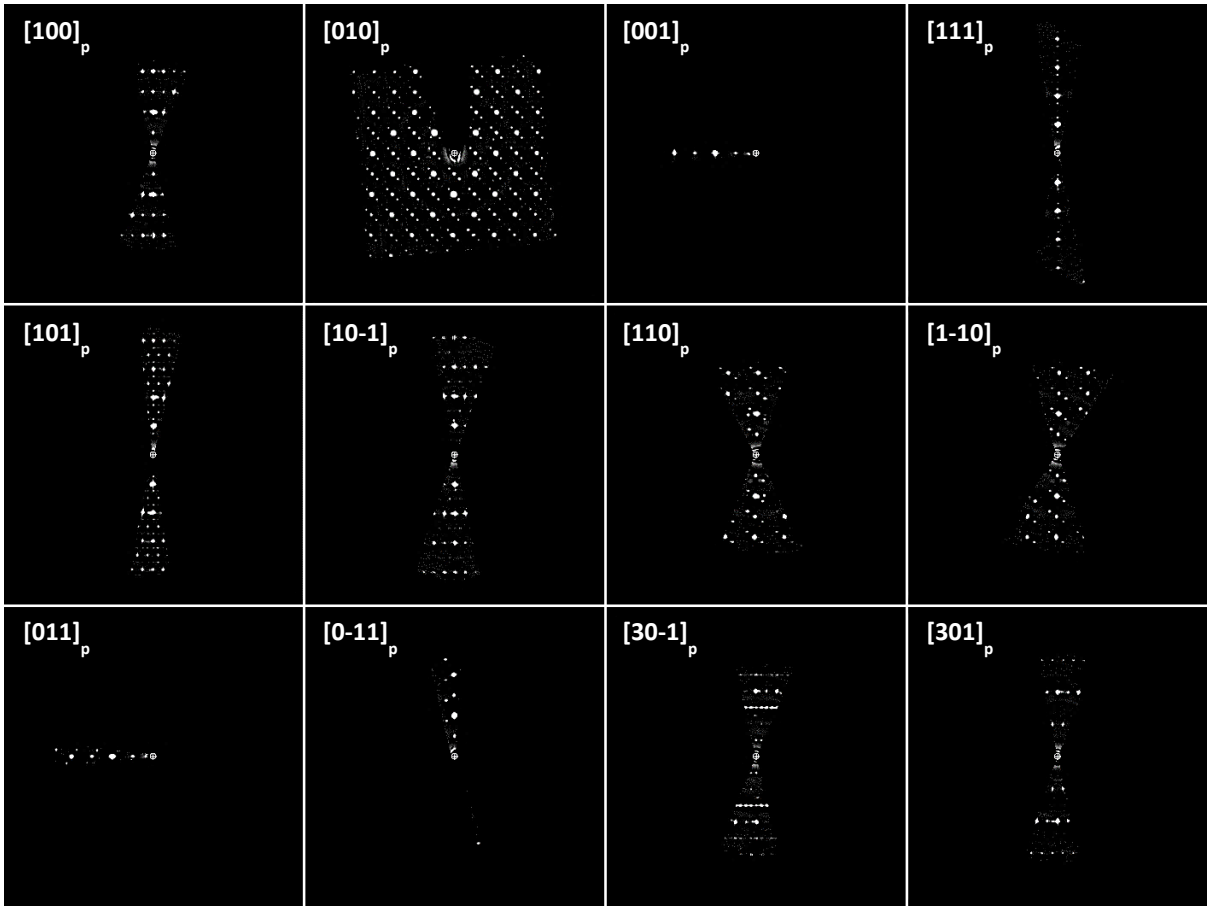

Figure S8. 3D ED sections of the small Cr1 crystal heated to 300°C in 33% O_2 in cycle 1. Tilting range was 36 degrees with a step of 0.5 degree.

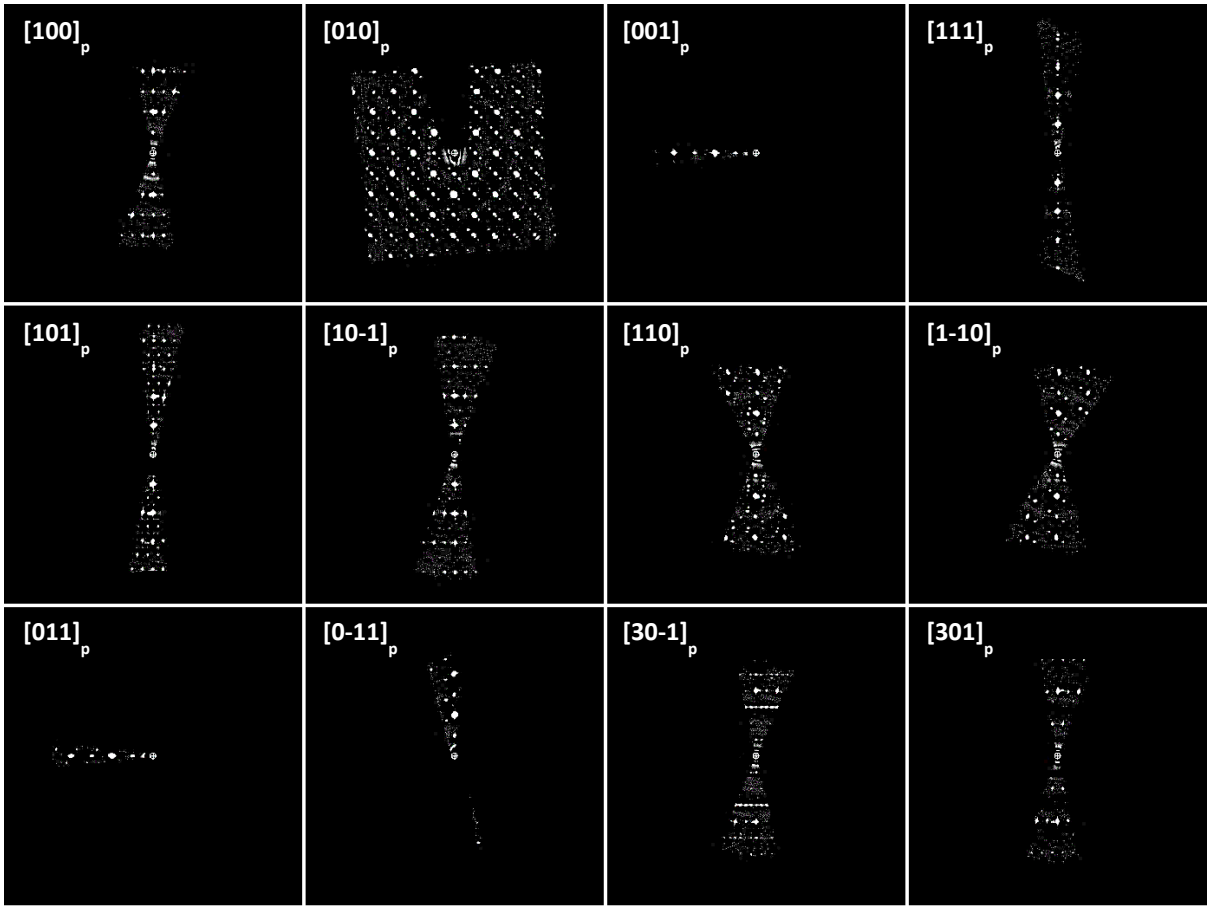

Figure S9. 3D ED sections of the small Cr1 crystal heated to 350°C in 33% O_2 in cycle 1. Tilting range was 36 degrees with a step of 0.5 degree.

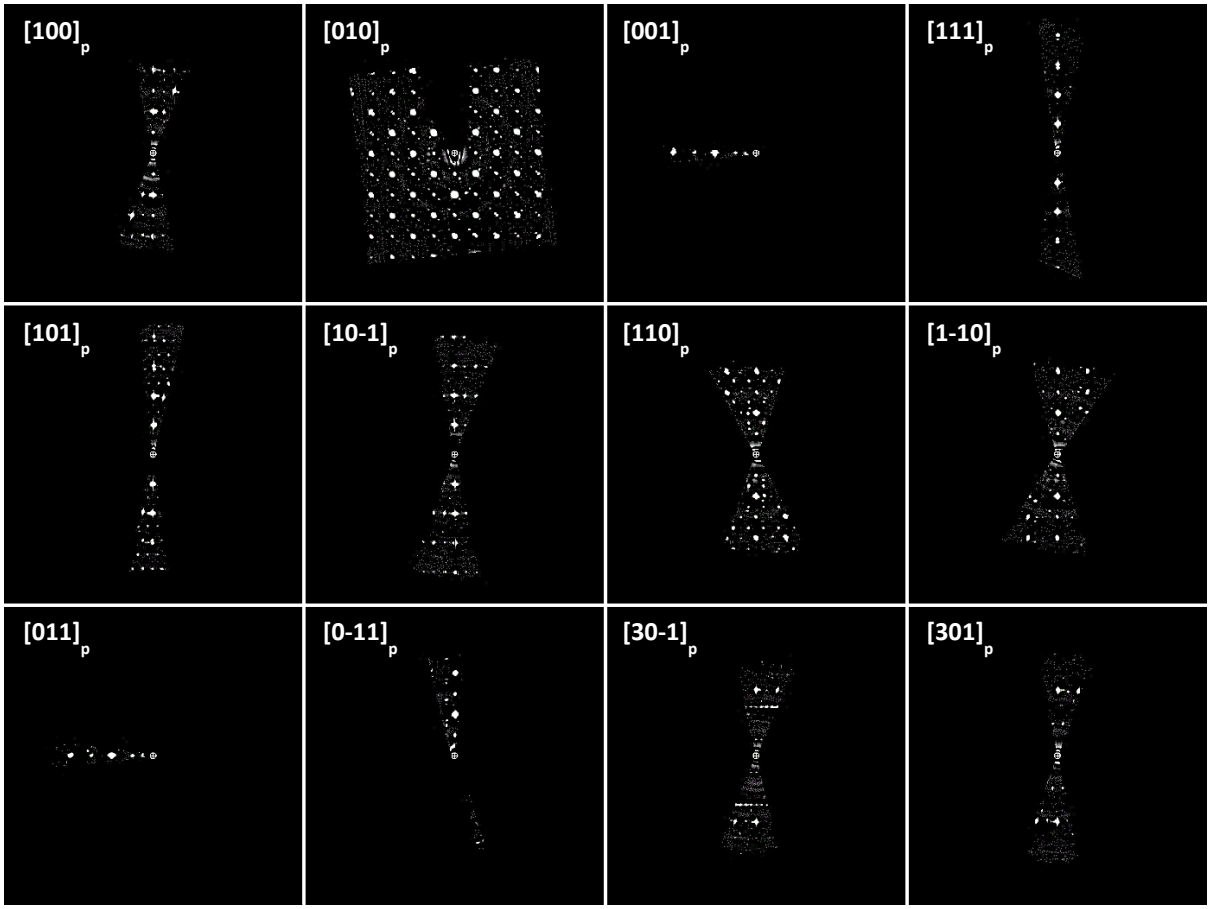

Figure S10. 3D ED sections of the small Cr1 crystal heated to 400°C in 33% O_2 in cycle 1. Tilting range was 36 degrees with a step of 0.5 degree.

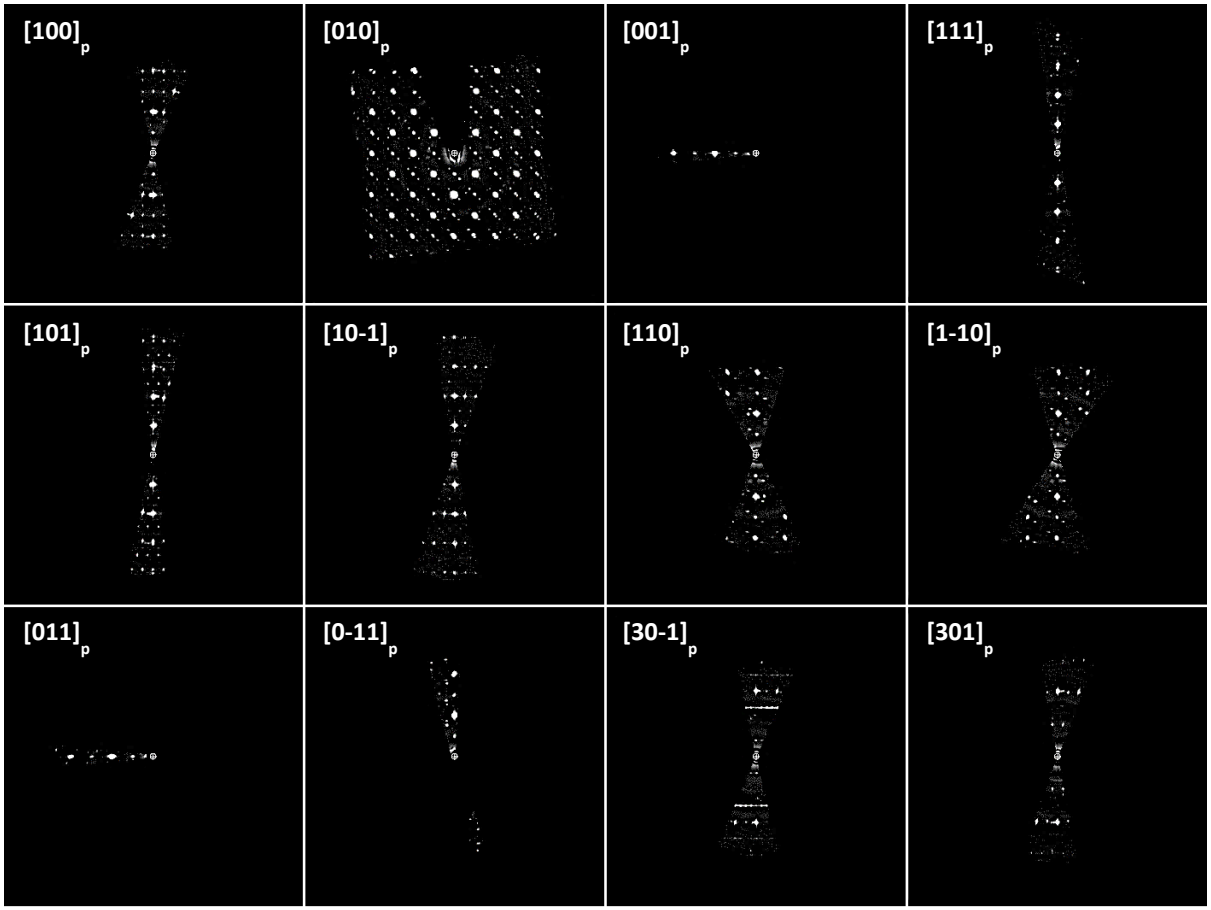

Figure S11. 3D ED sections of the small Cr1 crystal heated to 400°C in 33% O_2 and kept overnight in these conditions during cycle 1. Tilting range was 36 degrees with a step of 0.5 degree.

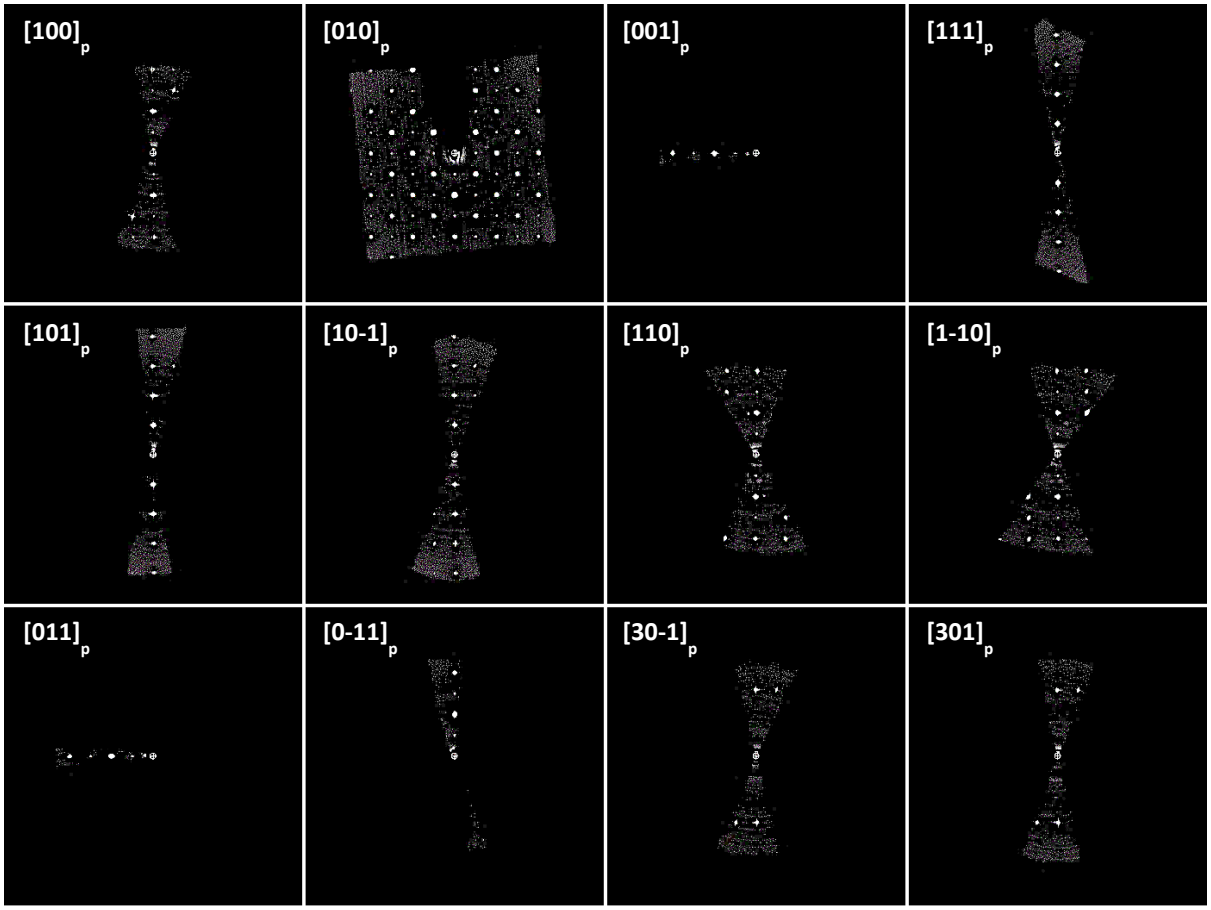

Figure S12. 3D ED sections of the small Cr1 crystal at 400°C in 100% O_2 in cycle 1. Tilting range was 38 degrees with a step of 0.5 degree.

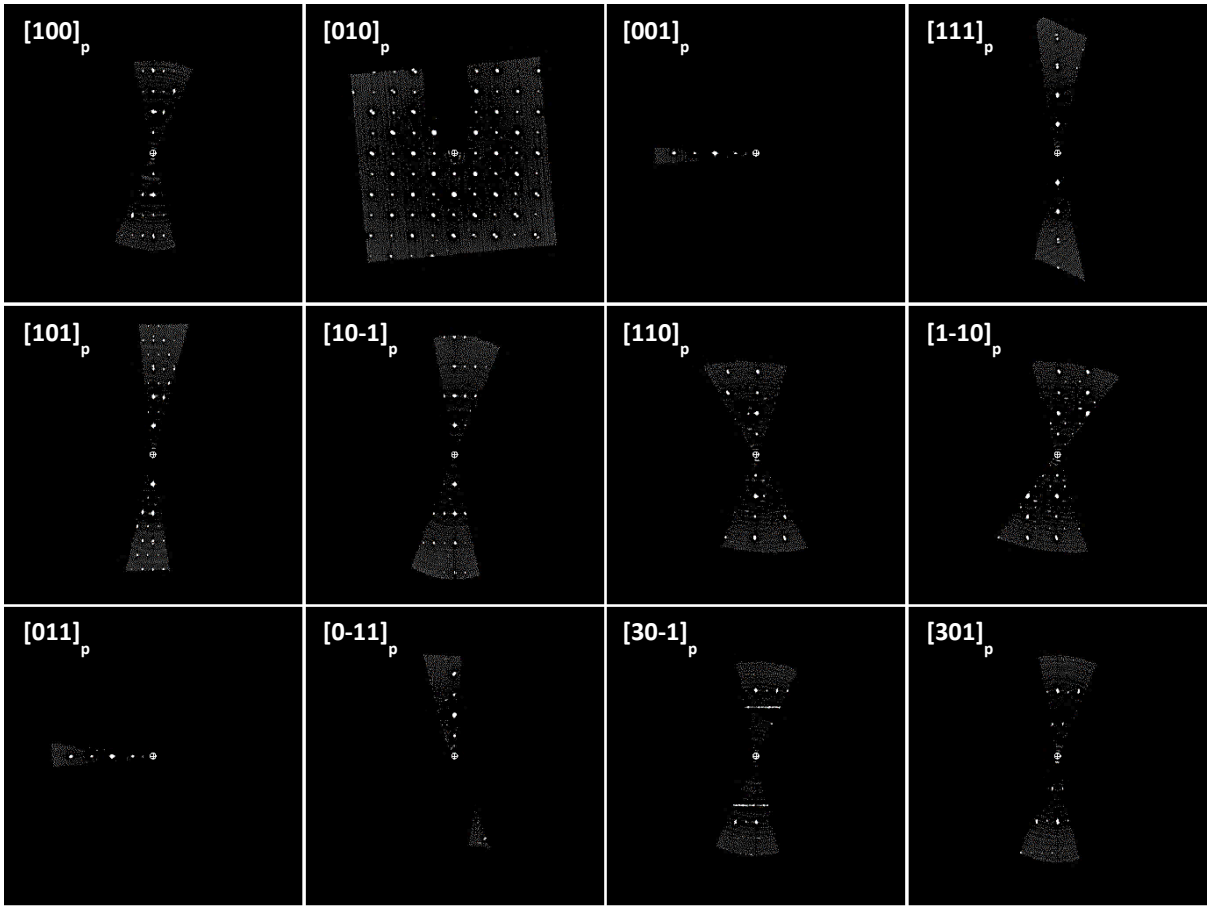

Figure S13. 3D ED sections of the small Cr1 crystal at cycle 2: heated to 200°C in 100% O_2. Tilting range was 38 degrees with a step of 0.5 degree.

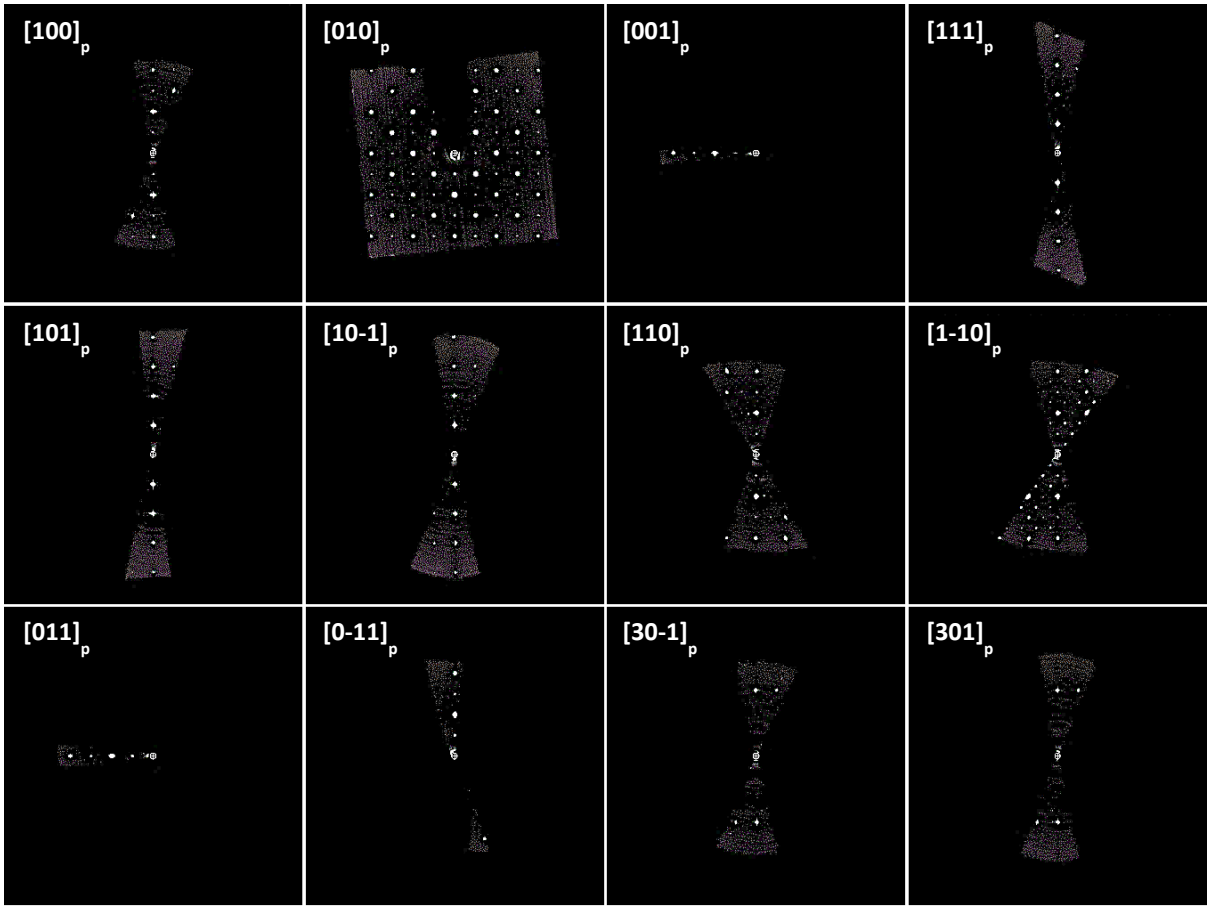

Figure S14. 3D ED sections of the small Cr1 crystal at cycle 2: heated to 400°C in 100% O_2. The data were acquired immediately after reaching the intended temperature. Tilting range was 38 degrees with a step of 0.5 degree.

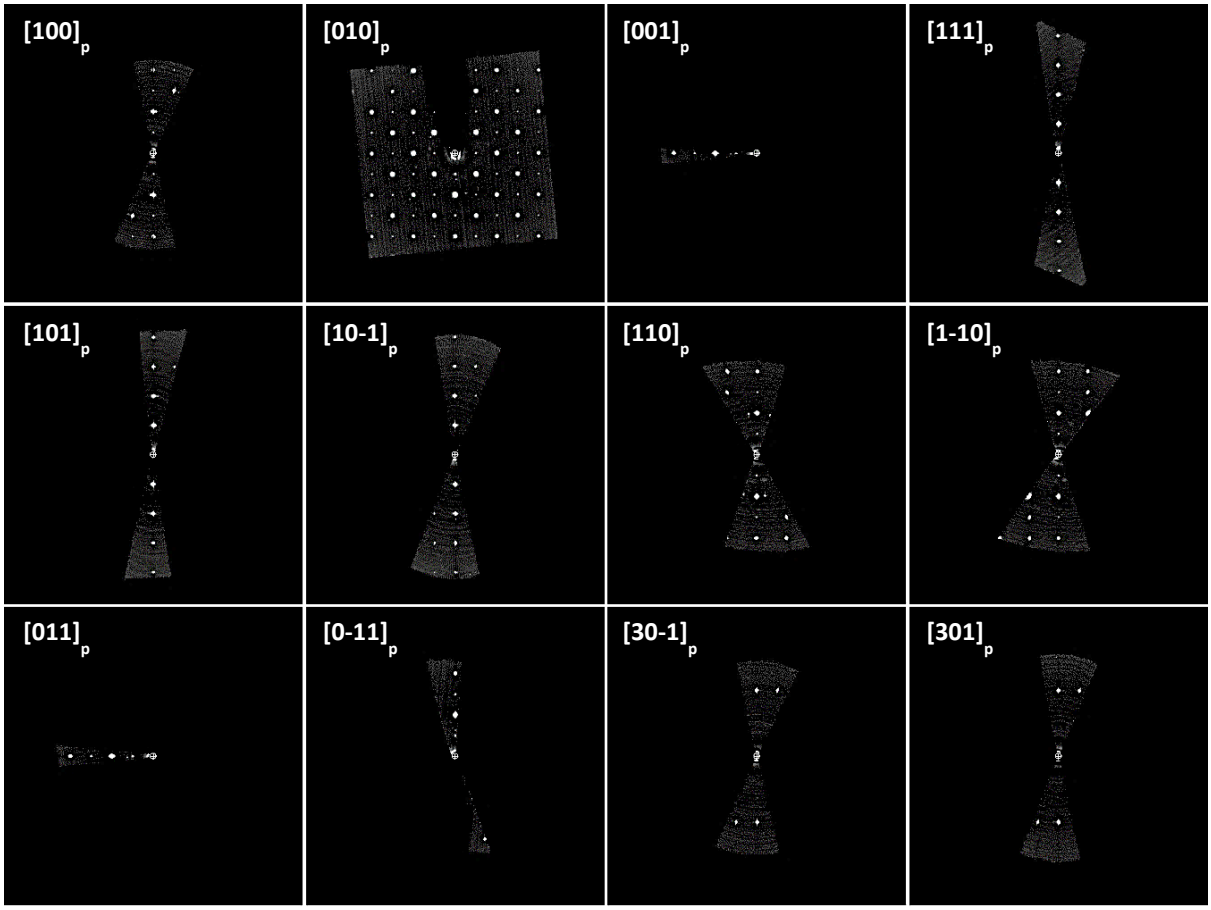

Figure S15. 3D ED sections of the small Cr1 crystal at cycle 2: heated to 400°C in 100% O_2. The data were acquired 40 minutes after reaching the intended temperature. Tilting range was 38 degrees with a step of 0.5 degree.

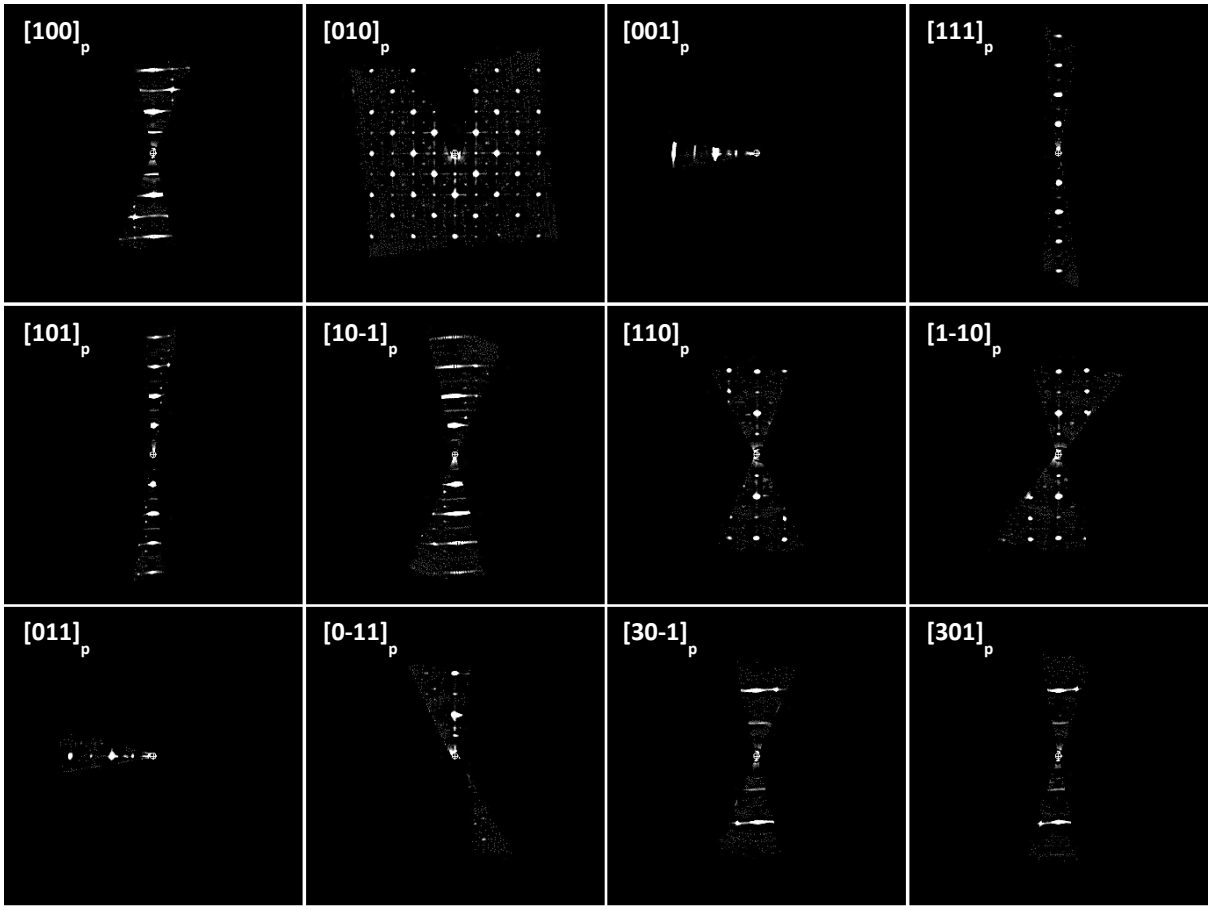

Figure S16. 3D ED sections of the small Cr1 crystal after cooling to RT in 100% O_2 at the end of cycle 2. Tilting range was 38 degrees with a step of 0.5 degree.

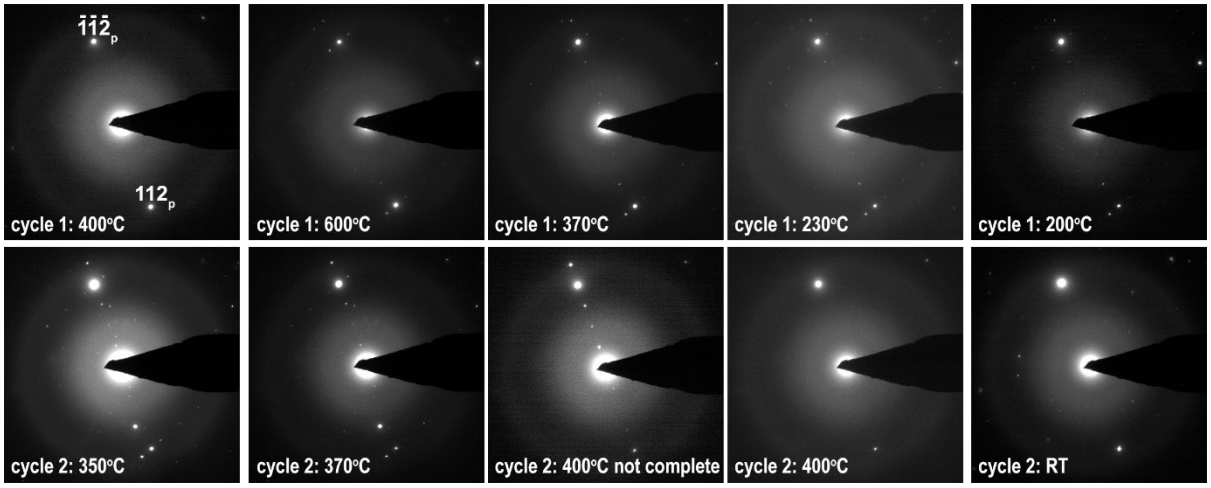

Figure S17. Out-of-zone ED patterns acquired from small crystal Cr1 along the same orientation at different conditions. The crystal transformed into cubic perovskite at 400°C in 100% O_2 so only basic reflections are visible (cycle 1: 400°C). Upon further heating (cycle 1: 600°C), satellite reflections appeared. The crystal was cooled down and patterns at intermediate temperatures were taken (cycle 1: 370°C and cycle 1: 230°C). At 200°C a 3D ED series was acquired and the crystal was heated again (cycle 2: 350°C and cycle 2: 370°C). The transformations became visible at 400°C (cycle2: 400°C). At the end of the experiment, the crystal was quenched to RT (cycle 2: RT).

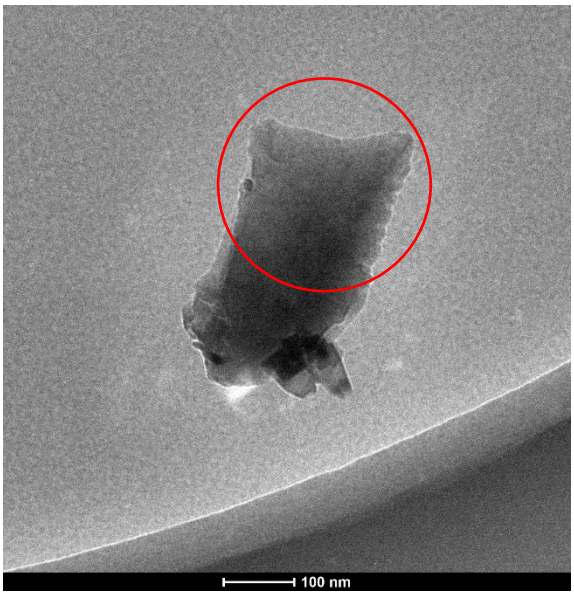

Figure S18. Overview TEM image of the small crystal Cr2. Red circle corresponds approximately to the position and size of the used selected area aperture.

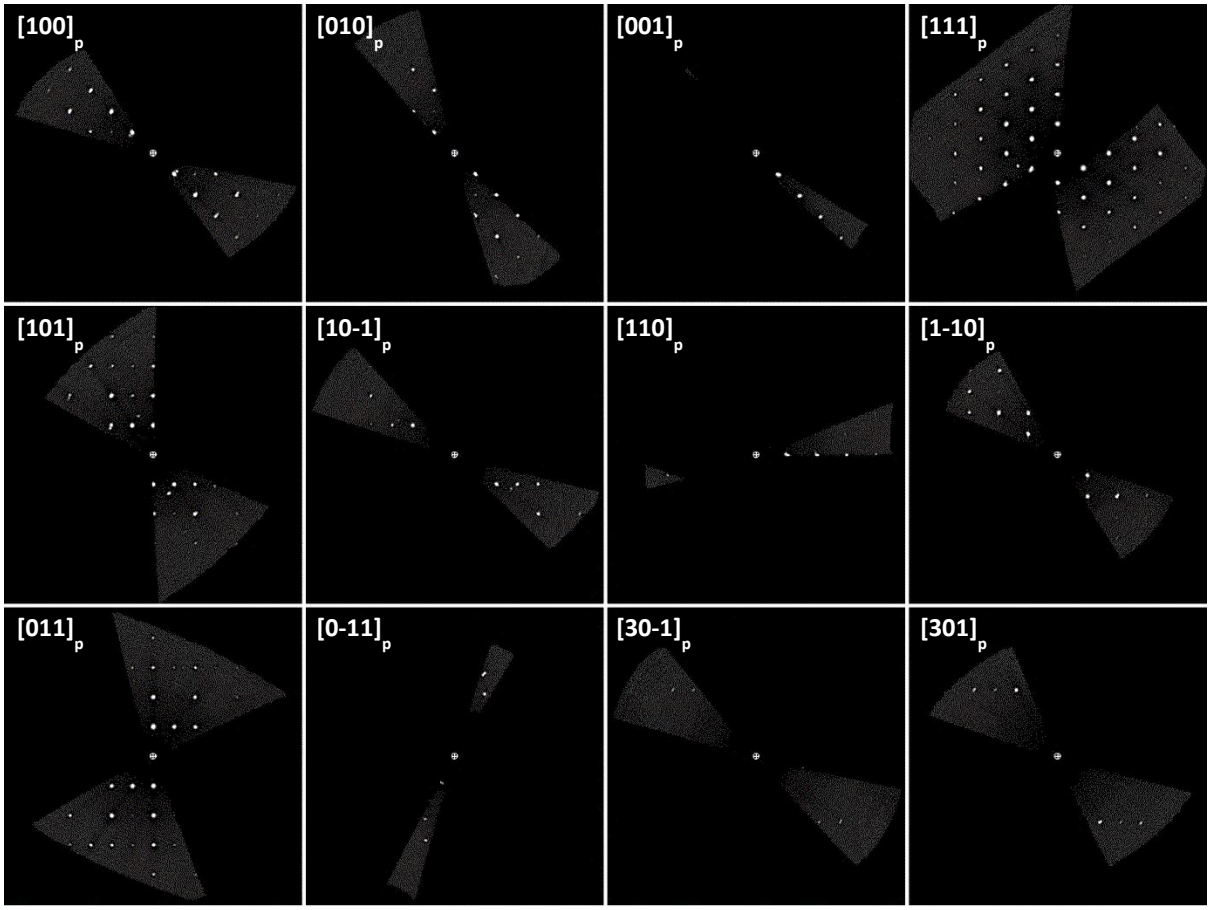

Figure S19. 3D ED sections of the small crystal Cr2 heated to 300°C in 10% O_2. Tilting range was 41 degrees with a step of 0.5 degree. The reconstructed sections match those of perovskite *Pm*-3*m*.

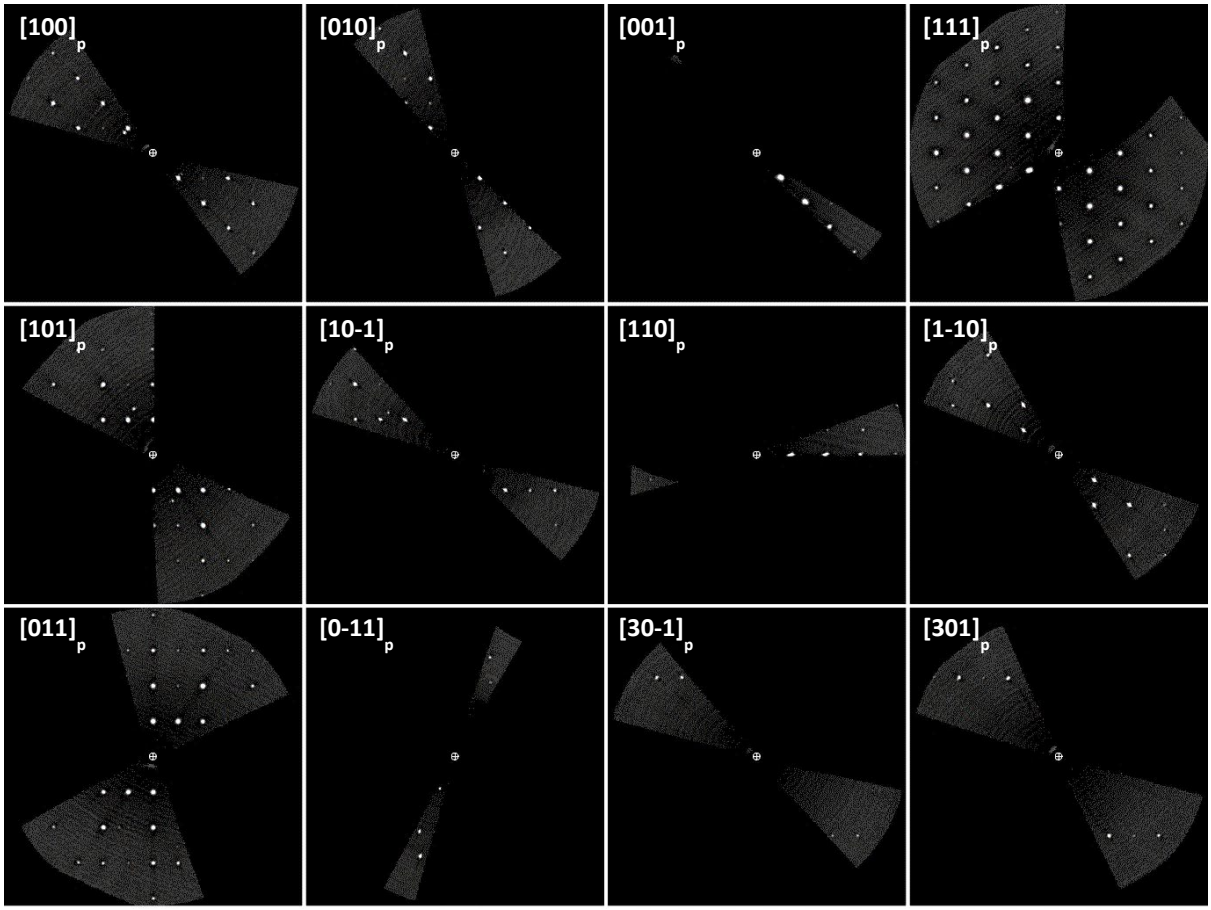

Figure S20. 3D ED sections of the small crystal Cr2 heated to 500°C in 100% O_2. Tilting range was 41 degrees with a step of 0.5 degree. The reconstructed sections match those of perovskite *Pm*-3*m*.

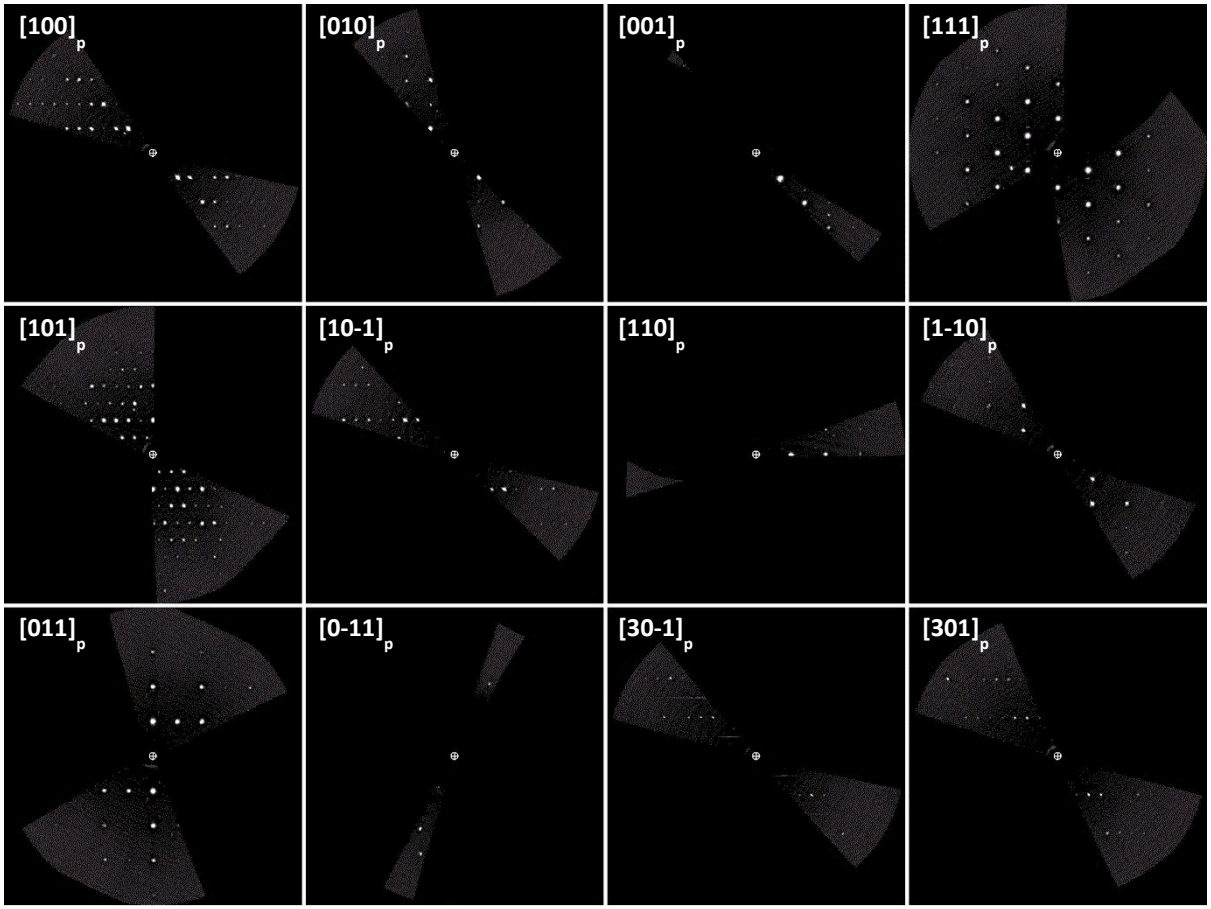

Figure S21. 3D ED sections of the small oxidized crystal Cr2 heated to 700°C in 10% H_2. Tilting range was 41 degrees with a step of 0.5 degree. The reconstructed sections match those of brownmillerite *Imma*.

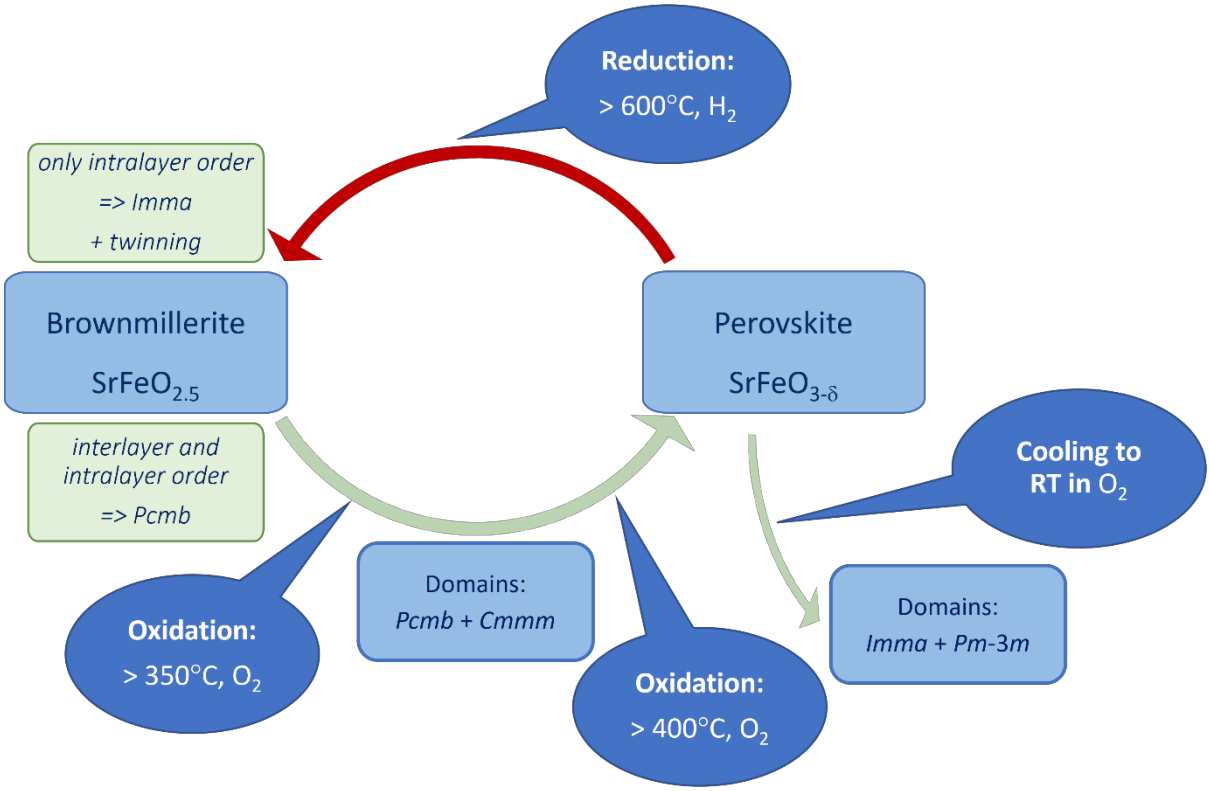

Figure S22. A scheme summarizing the *in situ* transformation of the brownmillerite $SrFeO_{2.5}$: upon heating in oxygen first the domains of the *Cmmm* structure begin to form and grow and a further heating leads to the formation of the perovskite structure. The perovskite structure can be reduced either by heating in hydrogen or by cooling in oxygen.

References

1 J. E. Auckett, A. J. Studer, N. Sharma and C. D. Ling, *Solid State Ionics*, 2012, **225**, 432–436.

2 J. P. P. Hodges, S. Short, J. D. D. Jorgensen, X. Xiong, B. Dabrowski, S. M. M. Mini and C. W. W. Kimball, *J. Solid State Chem.*, 2000, **151**, 190–209.