## Supplementary Materials

# High-Temperature Evolution of the Incommensurate Composite Crystal $Ca_{0.83}CuO_2$

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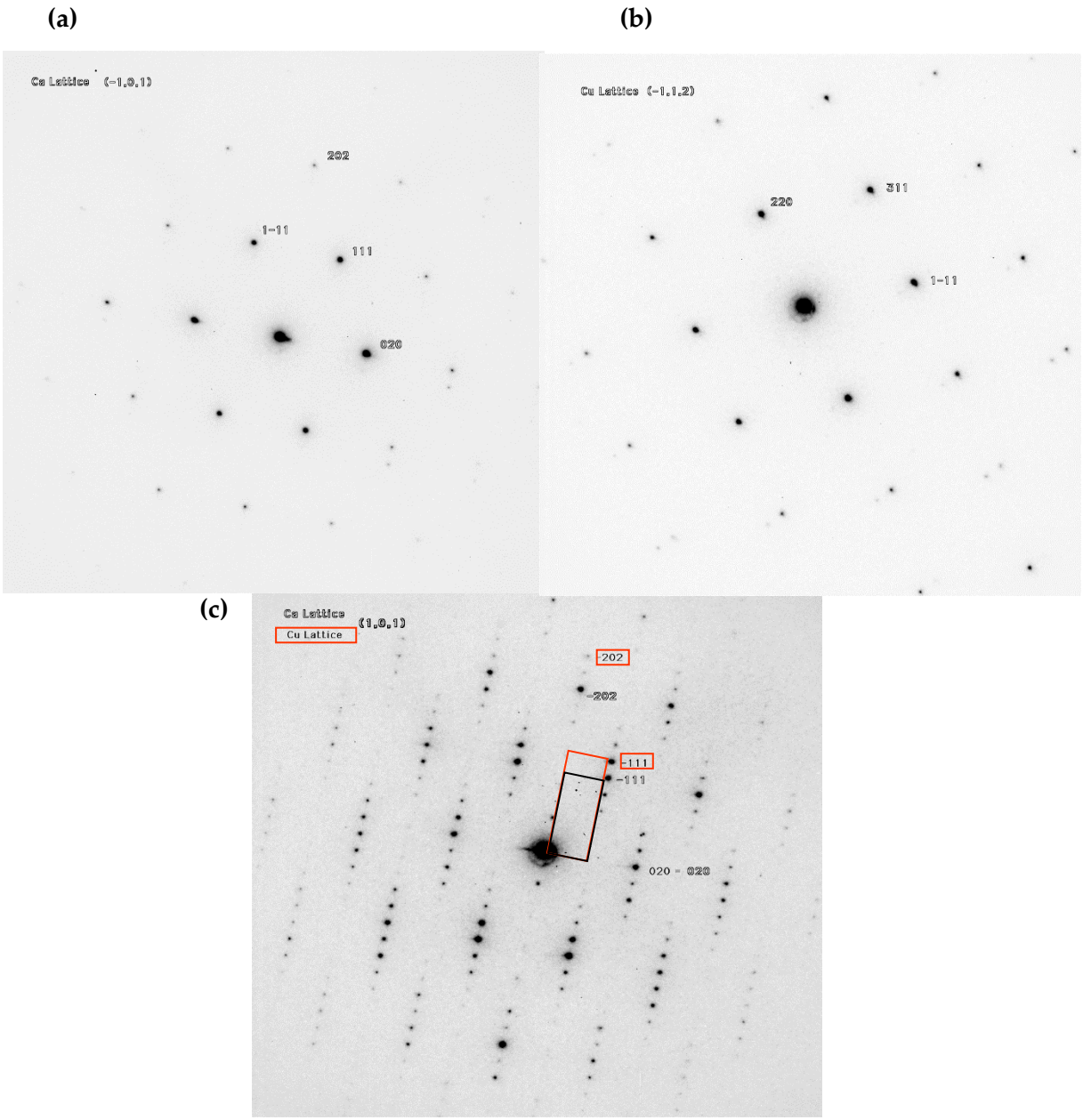


**Figure S1.** A collection of ED patterns of $Ca_xCuO_2$ compound: a) projection corresponding to [1-10] zone axis of the Ca lattice of the composite crystal, where no reflection of the $CuO_2$ sublattice is observed; b) [1-10] zone axis of the $CuO_2$ lattice in the composite crystal, where no reflection of the Ca sublattice is observed; c) [101] zone axis; the full indexing of the pattern is achieved by considering the interpenetration of Ca and $CuO_2$ subsystems.

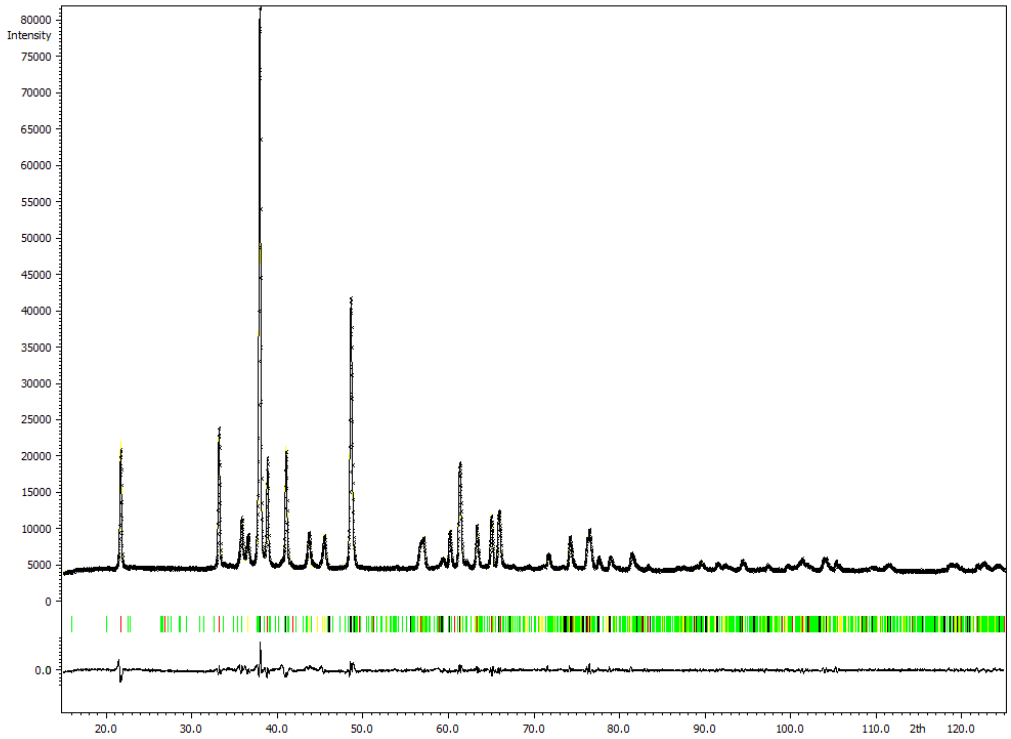


**Figure S2**. Rietveld plot obtained from the structural refinement of the (3D+1)-dimensional structure of composite crystal $Ca_{0.83}CuO_2$ on PXRD data collected at RT.

**Table S1.** Refined amplitudes of the Fourier expansion associated to each atomic positions in the $Ca_{0.83}CuO_2$ (3D+1)-dimensional structure. The parameters fixed to zero are forbidden by symmetry and are not considered during the refinement.

| Atom type | | A1 | B1 | A2 | B2 |
|---|---|---|---|---|---|
| Cu | | | | | |
| | x | 0 | 0 | -0.0048(17) | 0.018(2) |
| | y | 0.0065(10) | -0.0134(3) | 0 | 0 |
| | z | 0 | 0 | -0.0082(9) | -0.0018(25) |
| O1 | | | | | |
| | x | 0 | 0 | -0.012(7) | 0.034(7) |
| | y | 0.053 | 0.064(3) | 0 | 0 |
| | z | 0 | 0 | -0.0125(44) | 0.004(5) |
| O2 | | | | | |
| | x | 0 | 0 | 0.0039(77) | -0.0209(82) |
| | y | -0.0370(28) | 0.0434(23) | 0 | 0 |
| | z | 0 | 0 | -0.0104(48) | -0.0059(47) |
| Ca | | | | | |
| | x | 0.0197(41) | 0 | -0.020(1) | 0 |
| | y | -0.0086(90) | 0 | -0.0046(25) | 0 |
| | z | -0.0033(30) | 0 | -0.0060(20) | 0 |

**Table S2**. Crystal data for the monoclinic commensurate model of $Ca_5Cu_6O_{12}$. The ADP parameters are calculated on the basis of the basic undistorted structure.

| | | | | | |
|---|---|---|---|---|---|
| Space group | | $P2_1/a$ | | | |
| Cell constants | | a= 16.807 Å, b= 6.3196 Å, c= 5.4736 Å, β=104.93 ° | | | |
| Chemical formula | | $Ca_5Cu_6O_{12}$ | | | |
| Atom type (Labels) | WCK | x | y | z | ADP (Å2) |
| Ca1 | 2a | 0.000 | 0.000 | 0.000 | 0.0099 |
| Ca2 | 4e | 0.209 | 0.992 | 0.987 | 0.0099 |
| Ca3 | 4e | 0.409 | 0.998 | 0.005 | 0.0099 |
| Cu1 | 4e | 0.039 | 0.252 | 0.498 | 0.0025 |
| Cu2 | 4e | 0.209 | 0.240 | 0.496 | 0.0025 |
| Cu3 | 4e | 0.376 | 0.238 | 0.506 | 0.0025 |
| O1 | 4e | 0.111 | 0.179 | 0.251 | 0.0033 |
| O2 | 4e | 0.272 | 0.253 | 0.268 | 0.0033 |
| O3 | 4e | 0.429 | 0.324 | 0.234 | 0.0033 |
| O4 | 4e | 0.148 | 0.279 | 0.742 | 0.0025 |
| O5 | 4e | 0.311 | 0.226 | 0.723 | 0.0025 |
| O6 | 4e | 0.477 | 0.196 | 0.749 | 0.0025 |

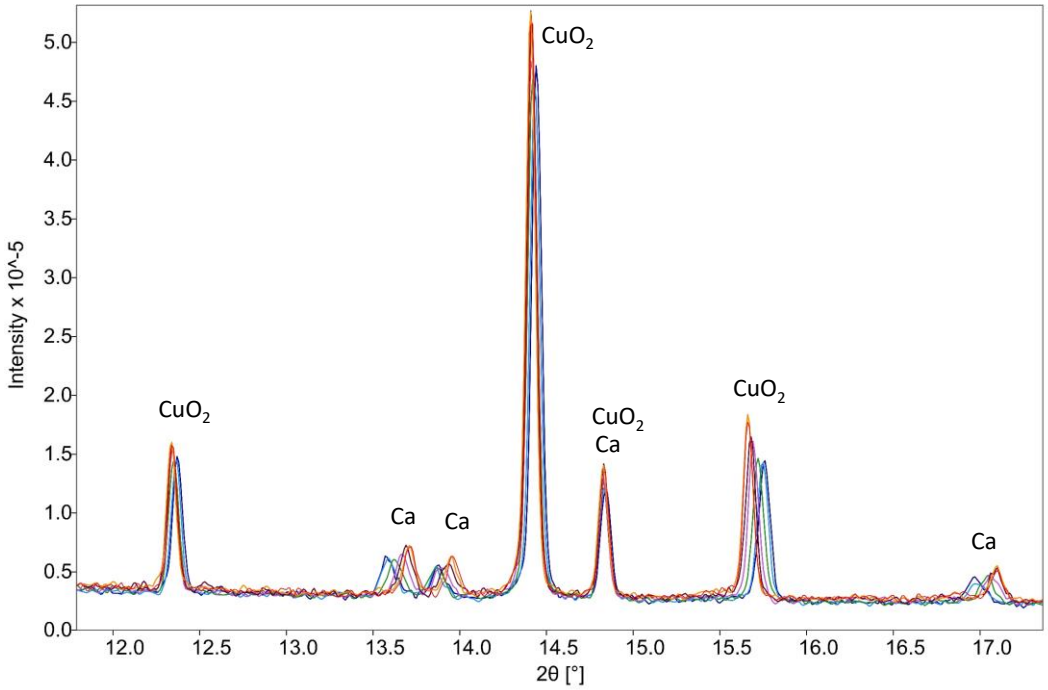


**Figure S3**. Synchrotron diffraction patterns collected from 320K to 950K (cold colors-lower temperature; warm colors-high temperature). The reflections associated to the Ca sub-structure manifest a progressive shift towards higher 2θ angles indicating the unusual shrinking of the lattice volume as the temperature increases. The $CuO_2$ sub-lattice shows the expected opposite trend.

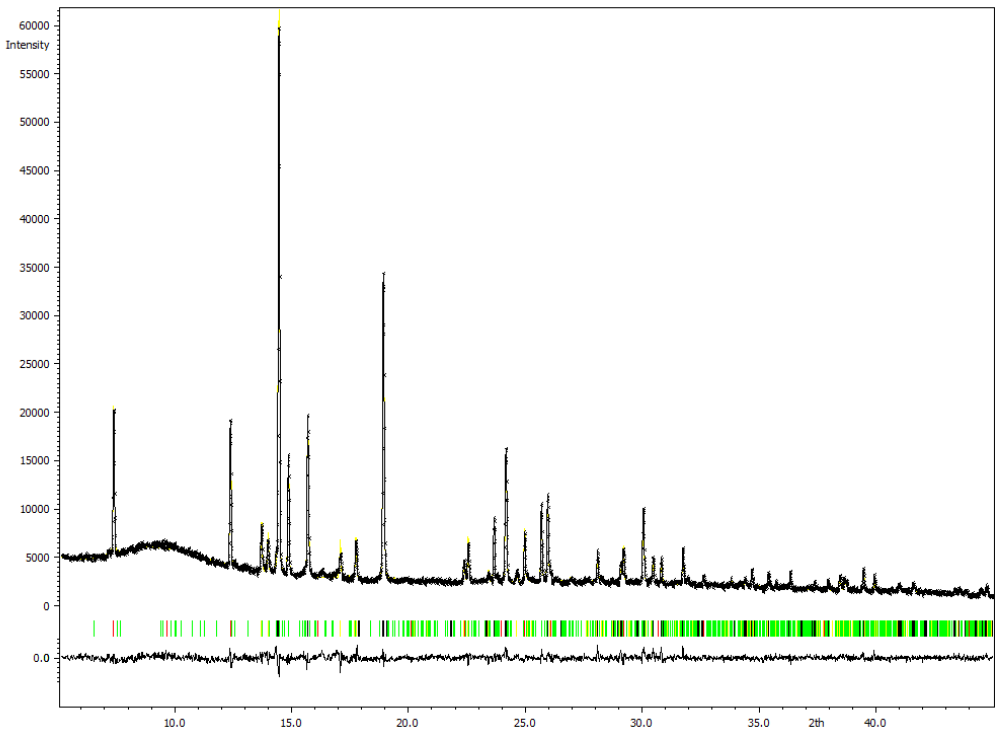


**Figure S4.** Rietveld plot obtained from the structural refinement of the Ca-based composite crystal on synchrotron diffraction data (λ=0.685Å) collected at 890K. The bump observed at around 10° of 2θ is related to the contribution of the glass tube containing the sample.

**Table S3**. Crystal data for the triclinic commensurate model of $Ca_6Cu_7O_{14}$ obtained for the diffraction data collected at 890K.

| | |
|---|---|
| Space Group | P-1 |
| Cell constants | a= 19.9247Å, b=6.3259Å, c=5.623Å, $\alpha$=90°, $\beta$=104.86°, $\gamma$=90° |
| Chemical Formula | $Ca_6Cu_7O_{14}$ |

| Label | x | y | z | Occupancy factors | ADP (Å^2) |
|---|---|---|---|---|---|
| Ca1 | 0 | 0 | 0 | 0.5 | 0.0316 |
| Ca2 | 0.17126 | 0.00112 | 0.97781 | 1 | 0.0316 |
| Ca3 | 0.34707 | 0.00651 | 0.00488 | 1 | 0.0316 |
| Ca4 | 0.5 | 0 | 0 | 0.5 | 0.0316 |
| Ca5 | 0.07347 | 0.50489 | 0.99147 | 1 | 0.0316 |
| Ca6 | 0.23942 | 0.50441 | 0.01000 | 1 | 0.0316 |
| Ca7 | 0.41594 | 0.49951 | 0.01853 | 1 | 0.0316 |
| Cu1 | 0.03295 | 0.25849 | 0.49902 | 1 | 0.0261 |
| Cu2 | 0.18026 | 0.24776 | 0.49807 | 1 | 0.0261 |
| Cu3 | 0.32344 | 0.23871 | 0.50184 | 1 | 0.0261 |
| Cu4 | 0.46170 | 0.23817 | 0.50111 | 1 | 0.0261 |
| Cu5 | 0.60628 | 0.24654 | 0.49766 | 1 | 0.0261 |
| Cu6 | 0.75297 | 0.25751 | 0.49993 | 1 | 0.0261 |
| Cu7 | 0.89240 | 0.26283 | 0.50237 | 1 | 0.0261 |
| O1 | 0.09372 | 0.19093 | 0.24178 | 1 | 0.0515 |
| O2 | 0.23183 | 0.27710 | 0.26338 | 1 | 0.0515 |
| O3 | 0.36300 | 0.34286 | 0.26575 | 1 | 0.0515 |
| O4 | 0.51581 | 0.33870 | 0.24309 | 1 | 0.0515 |
| O5 | 0.66592 | 0.26774 | 0.25080 | 1 | 0.0515 |
| O6 | 0.79560 | 0.18343 | 0.27003 | 1 | 0.0515 |
| O7 | 0.93707 | 0.14924 | 0.25376 | 1 | 0.0515 |
| O8 | 0.12591 | 0.26041 | 0.77492 | 1 | 0.0409 |
| O9 | 0.26900 | 0.23782 | 0.72744 | 1 | 0.0409 |
| O10 | 0.41828 | 0.22440 | 0.72355 | 1 | 0.0409 |
| O11 | 0.55805 | 0.23026 | 0.77276 | 1 | 0.0409 |
| O12 | 0.69585 | 0.25098 | 0.75475 | 1 | 0.0409 |
| O13 | 0.84405 | 0.27097 | 0.71355 | 1 | 0.0409 |
| O14 | 0.98958 | 0.27516 | 0.74990 | 1 | 0.0409 |