High-Temperature Evolution of the Incommensurate Composite Crystal Ca$_{0.83}$CuO$_2$

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Abstract: The crystal structure of the composite crystal Ca$_{0.83}$CuO$_2$ was investigated by synchrotron powder diffraction at high temperature. The incommensurate modulated structure was firstly analyzed at room temperature (RT) and successfully solved by adopting the (3D + 1)-dimensional symmetry P2$_1$/m(α0γ)0s. The composite crystal is featured by a non-uniform distribution of Ca ions occupying octahedral sites formed by the spatial arrangement by the infinite 1D CuO$_2$ chains. By approaching 500 K, Ca$_{0.83}$CuO$_2$ undergoes a structural rearrangement ruled by the shrinking of the Ca interatomic distances. The high-temperature crystalline phase is characterized by a different incommensurate periodicity requiring the recombination of the Ca/CuO$_2$ balance featuring the composite intergrowth of the two almost independent sub-structures. We ascertain that the new crystalline form is stable up to 950 K near to the limit of the thermal decomposition.

Keywords: composite crystals; Ca-based cuprates; incommensurate modulation; powder synchrotron diffraction study

1. Introduction

The study of the phase diagrams involving copper oxide CuO and alkaline or alkaline earth oxides demonstrated the occurrence of phases characterized by common structural features with general formula A$_x$CuO$_2$, where typically x = 1 for A = Na, K and 0.67 < x < 0.90 for A = Ca, Sr, Ba. Alkaline-based cuprates, like NaCuO$_2$ and KCuO$_2$, consist of alkaline layers [1–4] interpenetrated by edge-sharing CuO$_2$ ladders. The different size of Na and K cations, rules the periodic arrangement CuO$_2$ stripes and cations. Octahedral sites, formed by oxygen atoms of adjacent CuO$_2$ chains, are occupied by the alkaline cations in a 1:1 ratio with the CuO$_2$ units. For A = Ca$^{2+}$, Sr$^{2+}$ or Ba$^{2+}$, the structure remains strictly related to that of the corresponding alkaline-based compounds but, as a result of the increased atomic size, only a fraction of the octahedral sites is occupied and the compound results to be non-stoichiometric. Indeed, as the ionic radii of the alkaline-earth increases, A$^{2+}$/Cu decreases progressively as evidenced by the compositions reported in literature [5–8] and summarized in Table 1. The remarkable compositional flexibility is demonstrated by the occurrence of Na-based compounds with chemical composition Na$_{1.66}$CuO$_2$ showing a stable excess of Na$^+$ ions [9]. So far, K-based off-stoichiometric K$_{1.5}$CuO$_2$ can be efficiently fabricated [10], being the inferior content of K likely ascribable to the similar correlation between ionic radii and chemical composition observed for the alkaline-earth group of cuprates. Nevertheless, several structural studies accounted that this family of
cuprates represent a prototypical example of composite crystal [11–13]. Indeed, the crystalline phase is composed of two distinct sub-structures associated to the A cations and CuO$_2$ symmetries, respectively. The different symmetry and periodicity of the two sub-systems give rise to incommensurate displacive modulation observed in all the off-stoichiometric compounds [9,10,14–18]. The mismatch of the two sub-units, ruling the A/Cu balance, is generally confined to a single fundamental periodicity giving rise to a mono-dimensional incommensurate modulation.

| A         | x            | Effective Ionic Radii ($r_e$) |
|-----------|--------------|------------------------------|
| Ca$^{2+}$ | 0.83–0.85    | 1.00                         |
| Sr$^{2+}$ | 0.73         | 1.18                         |
| Ba$^{2+}$ | 0.67–0.70    | 1.35                         |

It is worth to recall that, similarly to the Cu-based family, a series of 1D layered compounds showing similar incommensurate modulated structure was discovered for alkaline and alkaline-earth cobalt oxides [19,20]. The layered Na$_{0.83}$CoO$_2$ composite crystal crystalizes in a triclinic symmetry and possess interesting thermoelectric properties [20].

The occurrence of infinite edge-sharing CuO$_2$ chains is a structural character of few materials and a series of unusual physical and chemical properties are featuring this family of compounds. Ordered mono-dimensional 1D spin arrangement was found in the SrCu$_2$O$_3$ and Sr$_{14}$Cu$_{24}$O$_{41}$ compounds [21–23]. The antiferromagnetic (AFM) ordering observed in Sr$_{14}$Cu$_{24}$O$_{41}$ below 60 K has been related to the spin orientation predominantly perpendicular to the 1D CuO$_2$ chains [22]. This is confirmed by the observation of similar antiferromagnetic coupling in Sr$_{17.73}$Cu$_2$O$_2$ [5,24], below 10 K. Analogously, incommensurately modulated calcium cuprates are characterized at low temperature by AFM coupling [17]. The magnetic properties of such cuprates show a complex behavior associated to the interplay of different 1D spin configurations (spin dimers, alternating Heisemberg chains, etc.). The off-stoichiometry is compensated by hole-doping of the cuprate ribbons with the proper balance of Cu$^{2+}$/Cu$^{3+}$ ratio. Interestingly, the Cu valence is not randomly distributed, but it is observed charge ordering giving rise to periodic magnetic correlations [25]. Recent inelastic neutron scattering studies on (Ca,Y)$_{0.82}$CuO$_2$ disclosed complex ferromagnetic frustrated interactions involving adjacent CuO$_2$ chains having a mono-dimensional (1D) AFM ordering [26].

Nevertheless, the Ca$_{0.83}$CuO$_2$ system exhibits a remarkable activity in the catalytic oxidation of volatile organic compounds, as well as the unusual ability to adsorb gases such as NOx, CO, CO$_2$, with strong selectivity toward NOx [27]. The reversibility of the sorption process, induced by thermal treatments, could make Ca$_x$CuO$_2$ with 0.824<x<0.84 a suitable material for de-NOx applications [27,28]. Furthermore, Ca-based cuprates gathered increasing attention in the field of nanocatalysis for the synthesis of different aromatic aldehydes, in solvent-free modes [29]. These novel applications demand the knowledge of the structural properties at the high-temperature regime suitable for catalytic and gas up-taking applications. Up to now, the structural studies of the off-stoichiometric cuprates was dedicated to the low temperature properties. In this work we present valuable insights obtained by the structural analysis of the Ca$_{0.83}$CuO$_2$ compound carried out by increasing the temperature up to 1073 K. The detailed structure determination of such complex incommensurate composite crystal was successfully achieved by introducing the superspace approach [13]. The experiments were performed adopting a time-resolved mode with a Debye–Scherrer diffractometer implemented in the BM08 beamline of ESRF large facility. The Rietveld refinements performed on the powder diffraction data unveil the complex evolution of the Ca$_{0.83}$CuO$_2$ composite crystal at high-temperature conditions.

2. Materials and Methods

Ca$_{0.83}$CuO$_2$ samples have been prepared following the technique of pyrolysis of a gel obtained from an acid solution of citrates of Cu and Ca metals. The starting reagents CaCO$_3$ and CuO are
dissolved by a concentrated solution of HNO₃. Afterwards, an excess of citric acid to the solution is added in order to form agglomerates with Ca and Cu metals. The prepared solution is then heated to remove water in order to obtain a colored blue gel. The further heating of the gel results in a pyrolysis where the organic components are removed. The final reactive amorphous powder is treated at 700 °C under flowing oxygen. Powder diffraction X-ray collected with a X’TRA diffractometer (Thermo Fisher, Switzerland) using a CuKα radiation, confirmed the successful synthesis of the cuprate excluding the presence of secondary phases. A high-resolution diffraction pattern collected with a low counting rate was used to perform the first structure refinement. The obtained crystallographic model was then adopted for the high-temperature structural investigation. Moreover, transmission electron microscopy (TEM) study was carried out with a Philips CM30T microscope (Philips, Germany) operating with 300 Kv. Electron diffraction (ED) patterns was collected using a Gatan slow-scan CCD camera (Philips, Germany).

The powder diffraction experiments were performed on the BM08 beamline at ESRF (European Synchrotron Radiation Facility, Grenoble, France) synchrotron with the radiation λ = 0.685 Å. A glass tube containing the sample was accommodated in a holder conveniently positioned over a gas blower heater. A translating imaging plate (IP) has been used to record the structural transition during the overall heating session. To couple the translating motion of the IP and the temperature change, a thermocouple was inserted in the vicinity of the polycrystalline sample. The integration of the diffraction patterns was carried out by defining time intervals corresponding to selected temperatures ranges (every 50 K). The heating system prevented a fine control of the temperature during the in-situ experiments, but we were able to collect diffraction patterns with suitable resolution in the range 400–950 K. The Rietveld refinements was undertaken with Jana2006 suite [30] by adopting the superspace approach [11–13].

3. Results and Discussion

In earlier works, ED and HREM investigations [14,15] addressed the structural study of Ca and Ba based cuprates. ED patterns manifest the typical features of composite crystals showing diffraction spots associated to two independent lattices. The indexing of the separated groups of the main reflections provided the following cell constants [15]:

(1) \( a = 2.80 \, \text{Å}, \ b = 6.32 \, \text{Å}, \ c = 10.57 \, \text{Å} \) (Orthorhombic Fmmm symmetry)
(2) \( a = 3.36 \, \text{Å}, \ b = 6.32 \, \text{Å}, \ c = 5.47 \, \text{Å}, \ \beta = 104.9° \) (Monoclinic C2/m symmetry)

The former is consistent with the typical arrangement of copper-oxygen chains in \( \text{La}_x\text{CuO}_2 \) compounds [14–16] and it is readily assigned to \( \text{CuO}_2 \) sublattice, the latter being clearly related to Ca sub-lattice periodicity. This interpretation agrees with the ED study that we performed on the samples fabricated and used for the high-temperature diffraction experiments. The indexing of spots observed in ED data by using Ca and \( \text{CuO}_2 \) reciprocal lattices is presented in the Supplementary Material Figure S1. As it is illustrated in the Figure 1, the composite crystal \( \text{Ca}_{0.83}\text{CuO}_2 \) is formed by the interpenetrating of the distinct lattices with their own translational symmetry. When the ratio of the unit cell volumes of the two sublattices is irrational, the two sub-structures coexist with off-stoichiometric compositions. The mutual interaction of Ca layers and \( \text{CuO}_2 \) ribbons is accompanied by structural modulation. As a result, the diffraction pattern of a composite crystal is the superimposition of the diffraction patterns of the two sublattices and satellite reflections. In the frame of the superspace approach the (3D + 1)-dimensional structure of a composite crystal, the first sub-unit is associated to the \( hkl0 \) indices, while the indices of the second one are given by \( 0klm \) with a shared reciprocal plane with indices \( 0kl0 \). Reflections \( hklm \) are the result of the mutual interaction of the two subsystems. The whole ED pattern is indexed by adopting the diffraction vector:

\[
H = ha^* + kb^* + lc^* + mq
\]
where \(a^*, b^*, c^*\) are related to one sub-lattice, whereas the modulation vector \(q = \alpha a^* + \beta b^* + \gamma c^*\) represents the incommensurate periodicity of the second sub-lattice. The incommensurate crystal structure of \(\text{Ca}_{0.83}\text{CuO}_2\) was solved by Miyazaki et al. [17] on the basis of both x-ray and neutron powder diffraction data. The composite crystal was represented by assigning the non-conventional space group \(\text{F2}/m(1+\alpha 0\gamma)0s\) with a modulation vector assuming the form 

\[
q = x a^*_{\text{CuO}_2} + (1-x)c^*_{\text{CuO}_2}.
\]

Indeed, the authors converted the monoclinic Ca sub-lattice by adapting a F centered cell with the following constants: \(a = 3.36\,\text{Å}, b = 6.32\,\text{Å}, c = 10.59\,\text{Å}, \beta = 92.99^\circ\). This model represents the first application of the superspace formalism to the structure description of the \(\text{Ca}_{0.83}\text{CuO}_2\) incommensurate composite crystal at room temperature [17]. In the actual work, we define the composite crystal with a different approach based on the monoclinic lattice associated to the Ca lattice. This new setting is illustrated in Figure 1 wherein both \(\text{CuO}_2\) and Ca sub-units are referred to a monoclinic symmetry having the \(c\) constant coinciding with 5.47 Å, but with different monoclinic angle.

\[ \begin{bmatrix}
    a^*_{\text{Ca}} \\
    b^*_{\text{Ca}} \\
    c^*_{\text{Ca}} \\
    q_2
\end{bmatrix} =
\begin{bmatrix}
    0 & 0 & 0 & 1 \\
    0 & 1 & 0 & 0 \\
    0 & 0 & 1 & 0 \\
    1 & 0 & 0 & 0
\end{bmatrix}
\begin{bmatrix}
    a^*_{\text{CuO}_2} \\
    b^*_{\text{CuO}_2} \\
    c^*_{\text{CuO}_2} \\
    q_1
\end{bmatrix} \]

In this frame, the superspace symmetry for the \(\text{CuO}_2\) sub-structure is \(P2_1/m(\alpha 0\gamma)0s\), characterized by non-primitive translation conforming the \(m_s\) mirror. The symmetry rules define the modulation vector as 

\( \mathbf{q} = \alpha \mathbf{a}^* + \gamma \mathbf{c}^* \) having \(\alpha\) equivalent to both the \(x\) compositional parameter \(\text{Ca}_x\text{CuO}_2\) and the \(a_{\text{CuO}_2}/a_{\text{Ca}}\) fraction [14,15].

The fundamental undistorted structure of \(\text{CuO}_2\) is constituted by a special position for Cu and two independent positions for O with coordinates \((x, 1/4, z)\). The Ca atom is positioned at the origin of the second basic sub-structure. The modulation of the three atomic species was defined by the Fourier modulation function:

\[
u'(\bar{x}_4) = \sum_{n=1,2} A_n^x \sin(2\pi n\bar{x}_4) + B_n^x \cos(2\pi n\bar{x}_4) \]
where \(x_4\) represents the four-dimensional variable in the superspace, and the \(A^i\) and \(B^j\) parameters allowed by the symmetry are refined to determine the displacive modulation for each atomic site. To finely describe the modulation function of the atomic species, we introduced the first and second order of the cosine and sine components of the Fourier series.

The (3D + 1)-dimensional crystal data of the Rietveld refinement obtained from the RT diffraction data are summarized in the Table 2. The structural refinement achieved the agreement factors \(R_p = 2.26\%\) \(R_{wp} = 3.07\%\) and the Rietveld output plot is depicted in Supplementary Material Figure S2. The refined modulation vector \(q = 0.83057(7)a^* + 0.0032(3)c^*\) agrees with the nominal chemical composition. The \(a_{\text{CuO}_2}\) cell constant can be related to \(a_{\text{Ca}}\) with the simple relation \(6a_{\text{CuO}_2} = 5a_{\text{Ca}}\), from which \(a_{\text{CuO}_2}/a_{\text{Ca}} = 5/6 = 0.833\), therefore, the chemical formula could be suitably indicated as \(\text{Ca}_5\text{Cu}_6\text{O}_{12}\).

Table 2. Summarized crystal data for the (3D + 1)-dimensional crystal structure of \(\text{Ca}_{0.83}\text{CuO}_2\) composite crystal at RT.

| Sublattice | \(\text{CuO}_2\) | \(\text{Ca}\) |
|-----------|----------------|----------------|
| Space Group | \(P2_1/m(a\overline{a}0\gamma)0\) | \(P2_1/a(a\overline{a}0\gamma)0\) |
| Crystal system | Monoclinic | Monoclinic |
| Unit Cell (Å,°) | \(a = 2.8010(5)\) | \(a = 3.3277(5)\) |
| | \(b = 6.3193(1)\) | \(b = 6.3193(1)\) |
| | \(b = 5.4734(9)\) | \(c = 5.4734(9)\) |
| | \(\beta = 104.939(4)\) | \(\beta = 105.040(4)\) |
| \(q\) | \(0.83057(7)a^* + 0.0032(2)c^*\) | \(1.20144(7)a^* - 0.0038(6)c\) |
| Atomic position (\(x, y, z\)) | Cu1 \(\frac{1}{2} \frac{1}{2} \frac{1}{2}\) | Ca1 0 0 0 |
| | O1 \(0.625(4)\) | O2 \(0.252(2)\) |
| | O2 \(0.875(5)\) | O2 \(0.741(2)\) |
| Isotropic ADP | Cu1 0.021(10) | Ca1 0.101(90) |
| | O1 0.033(32) | O2 0.025(35) |
| \(U_{iso}\) (Å\(^2\)) | | |
| Global R indexes | \(R\) 0.0187 | \(R_{wp}\) 0.0162 |
| Main Reflections | 0.0152 | 0.0147 |
| Composite part \(\text{Ca}\) | 0.0152 | 0.0147 |
| Composite part \(\text{CuO}_2\) | 0.0232 | 0.0194 |
| \(R_p\) | 0.0226 | |
| \(R_{wp}\) | 0.0307 | |

Table S1 resumes the refined values of the \(A^i\) and \(B^j\) amplitudes associated to the fractional basic coordinates. Concerning the Cu-O interactions, the four-fold coordination is far from the ideal planar configuration being perturbed by the propagation of a tilted wave along the ribbons. The Cu-O distances are characterized by an oscillating mean bond length ranging from 2.05 to 1.85 Å with a global average of 1.93 Å. The distortion of the \(\text{CuO}_2\) chains is related to the periodic charge ordering well described by plotting the modulated Cu-O lengths calculated from the (3D + 1)-dimensional model. The sequence of the in-phase shrinkages and expansions of the square coordination can be correlated with the mixed valence \(\text{Cu}^{2+}/\text{Cu}^{3+}\). The bond valence (BV) plot of Figure 2c demonstrates that the Cu oxidation alternates between 2+ and 3+ limits, with the same period of Cu-O modulated interactions. The assigned valence must be interpreted bearing in mind that, for such a complex structure, the bond valence evaluation is not straightforward. Therefore, the upper region of the curve approaching 2.9 value was attributed to 3+ valence, whereas the region of the curve ranging from 1.8 to 2.2 likely corresponds to \(\text{Cu}^{2+}\).
Figure 2. (a,b) Modulated Cu-O interactions versus internal incommensurate parameter \( t = x_4 - q \times i \) for RT and 890 K structures respectively. (c,d) BV summation obtained on the basis of the modulated Cu-O interactions for RT (c) and 890 K (d) phases. The red and green dotted curves represent gaussian functions used to fit the VB profile whilst the blue line corresponds to their convolution.

As a result, considering a commensurate six-fold periodicity, the CuO\(_2\) chains are constituted by the sequence Cu\(^{2+}\) - Cu\(^{2+}\) - Cu\(^{3+}\) - Cu\(^{2+}\) - Cu\(^{2+}\) - Cu\(^{3+}\). This charge ordering topology is in agreement with the spin hole arrangement formulated by M. Isobe at al. [18] for the Ca\(_{0.824}\)CuO\(_2\) composition and with former studies treating the Ca\(_{0.83}\)CuO\(_2\) magnetic properties [14–16].

Nevertheless, the wave-like modulation of oxygen sites determines the major distortions of the environment of Ca atoms with the occurrence of remarkably distorted octahedral sites (see Figure 3). In this sense, the mutual interplay of the two sub-units is essentially ruled by the displacive modulation of the oxygen sites.

Figure 3. Commensurate superstructure for Ca\(_5\)Cu\(_6\)O\(_{12}\). The graphical representation emphasizes the sequence of the three octahedral sites occupied by Ca\(^{2+}\).

The hypersection of the (3D + 1)-dimensional composite crystal [11] corresponding to \( q = 5/6a^* \) (the \( \gamma \) is approximated to 0 value) provides a commensurate superstructure having unit cell constants...
a = 6a_{\text{CuO}_2} = 5a_{\text{Ca}}, b = b_{\text{Ca}}, c = c_{\text{Ca}} and $\beta = 104.9^\circ$ with P2$_1$/a symmetry (the crystal data are reported in the Table S2). The structure model consists of three independent positions for Cu and Ca atoms, having general coordinates (x, $\frac{1}{4}$, $\frac{1}{2}$) and (x,0,0), respectively, and 6 sites for the oxygen atoms. The Figure 3 represents the commensurate five-fold superstructure where the Ca octahedral coordination and structural modulation of CuO$_2$ stripes are emphasized.

The sequence of edge-shared octahedra occupied by Ca$^{2+}$ is discontinuous and after the third occupied site, the successive ideal Ca site is vacant. This cluster is represented in the Figure 3 by the Ca2-Ca1-Ca2 labelling being the Ca2 site markedly distorted. The next two octahedral sites indicated as Ca3 are rotated of about 90° with respect the previous orientation. The Ca2 coordination is affected by a strong deviation from the regular octahedral condition with at least 7 Ca-O short interactions ranging around 2.08 Å.

The high-temperature trend recorded in synchrotron diffraction experiments highlights the almost independent thermal expansion of the two sub-structures constituting the composite crystal.

In the Supplementary Material Figure S3, the overlay of the diffraction patterns collected in the temperature range 320–950 K is shown. Interestingly, the reflections associated to Ca sub-lattice are progressively shifted towards high 2θ region as the temperature increases. For each temperature step, Rietveld refinements was undertaken. The monoclinic model with P2$_1$/m($0\alpha0\gamma$)0s is adopted for the overall temperature range and no change of symmetry of the (3D + 1)-structure was observed as it is indicated by the good agreement factors achieved for Rietveld refinements carried out for the high-temperature diffraction patterns (as an example see Supplementary Material Figure S4). The Figure 4 illustrates the evolution of the unit cell constants for both sub-lattices and corresponding change of the $q$ vector against temperature. Upon heating, the composite crystal undergoes an adaptive structural change featured by the shrinking of Ca sub-structure. The onset of this structural transition corresponds approximately to 540 K as it is well drawn by the change of the $q$ vector periodicity as well as the evolution of the $a$ lattice parameter for both sub-structures (see Figure 4 a,b). Conversely, as it is illustrated also by the Figure 4d, by increasing the temperature, the CuO$_2$ sub-unit expands as expected. Beyond 500 K, the $\alpha$ parameter of the $q$ modulation vector exhibits a marked increment moving from 0.830 to 0.851; the $\gamma$ component abruptly increases and relaxes beyond 700 K. The deviation from a commensurate 5/6 periodicity indicates a recombination of the compositional Ca/Cu ratio mediated by the oxygen modulation. This is particularly evident by plotting the Cu-O lengths calculated for the 890 K structure wherein the structural recombination of the Ca-O interactions impacts on the CuO$_2$ chains. The Figure 2b shows that the Cu-O modulated lengths are spanned in a broad range and the Cu environment departs from the periodic alternation of short/long interactions observed in the phase stable at RT. The BV evaluation reported in the Figure 2d indicates a complex distribution of the mixed valence 2+/3+ for Cu and the calculated curve is actually the convolution of two periodic wave-like periodicities. The additional curve introduced to fit the BV profile shows a maximal value around 2.3 and the convolution of the two calculated Gaussian profiles point out a consistent rising of the Cu$^{2+}$ content.

The average valence for Cu, extended throughout the incommensurate composite crystal, is around 2.28 with a slight but not negligible decrement with respect the oxidation state of 2.35 observed at room temperature. The shortening of the Ca-Ca distances rises the positive charge density in Ca$_x$CuO$_2$ compound which is, in turn, compensated by a decrease of Cu$^{3+}$ occupancy alongside CuO$_2$ ribbons. The complex curve of the BV summation can be also interpreted by recalling earlier studies related to the synthesis of such compound under unconventional conditions [31,32].
Figure 4. (a–d). Temperature dependence of the structural parameters featuring the modulated composite crystal Ca$_{0.83}$CuO$_2$. The red symbol/line is referred to the structure parameters of the Ca sub-structure whereas the blue one indicates the trend for CuO$_2$ part. The dimension of the symbols exceeds to e.d.s. for the refined parameters.

In particular, X.M. Qin and co-authors [32] explored high-temperature and high-pressure conditions to ascertain the stability of the off-stoichiometry Ca$_x$CuO$_2$ compounds. They accounted that, by crossing 1028 K, Ca$_{0.83}$CuO$_2$ decomposes into Ca$_2$CuO$_3$ + CaO at ambient pressure. Indeed, the additional curve convoluted in the BV periodicity could be related to the compositional instability, indicating an incipient phase separation of CaO and consequent formation of Ca$_2$CuO$_3$. Nevertheless, we did not notice the occurrence of CaO phase in the synchrotron diffraction pattern collected at high-temperature limit. Considering the crystal structure at 890 K, it is possible to define a new commensurate superstructure based on the broad assumption that for $q = 0.851a^* + 0c^* \approx 6/7a^*$ so as $6a_{\text{Ca}} \approx 7a_{\text{CuO}_2}$. The six-fold superstructure corresponding to the ideal Ca$_6$Cu$_7$O$_{14}$ composition has a triclinic P-1 symmetry with seven independent sites for Cu and Ca, respectively (see Table S3). Two symmetrically special sites of Ca atoms are occupied only by half in order to preserve compositional requirements. It is worth to stress that the new chemical formula is consistent to the redistribution of Ca and Cu cations across the average composite matrix and cannot be intended as a substantial increment of Cu amount. Hence, the chemical content remains constant but with a different spatial distribution over the average unitary crystal volume. In the six-fold supercell, depicted in Figure 5, the main difference with respect the RT structure relies on the more regular octahedral environments hosting Ca$^{2+}$ ions. Among the seven sites for Ca, only Ca6 is affected by a strong distortion of the oxygen coordination with the occurrence of 7 Ca-O short interactions. The Ca6 site can be thus associated to the Ca2 of the Ca$_5$Cu$_6$O$_{12}$ RT phase, but in the actual structure this complex environment involves only 1/7, rather than 1/3, of the occupied interstices. The CuO$_2$ ribbons show the wave-like distortion already observed at low temperature.
4. Conclusions and Future Perspectives

The crystal structure of the composite crystal Ca$_{0.83}$CuO$_2$ has been reinvestigated and characterized by synchrotron diffraction experiments at high-temperature conditions. We noticed that the incommensurate modulated structure undergoes a structural transition beyond 540 K. The intrinsic composite nature of the compound is particularly evident by observing the apparently independent evolution of the Ca and CuO$_2$ sub-structures upon the temperature increasing. The Ca-sublattice undergoes a progressive contraction of the volume mainly related to the adjustment of the Ca-Ca distances alongside the a vector. The crystal structure stable at high temperature is featured by a diverse displacive modulation for O1 and O2 defining relaxed octahedral sites if compared to the RT condition. The modulation vector $q = 0.8510(5)c^* + 0.013(4)a^*$ yields to a new compositional variant approaching the $a_{CuO_2}/a_{Ca} = 0.851$ ($6a_{Ca} = 7a_{CuO_2}$ in first approximation) lattice relationship. The progressive recombination of the two sub-structures forming Ca$_x$CuO$_2$ outlines the unique structural versatility of composite crystals in combining competing structural factors in the same phase. Such structural results suggest forthcoming investigations from RT to 1000 K to explore the physical and chemical properties characterizing the high-temperature phase. In this frame, we are setting in-situ diffraction experiments on composite Ca$_{0.83}$CuO$_2$ dealing with the dynamical up-taking of NOx gases in the 500–700 K temperature range.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/10/7/630/s1
High temperature evolution of the incommensurate composite crystal Ca$_{0.83}$CuO$_2$/s1, Figure S1: A collection of ED patterns of Ca$_x$CuO$_2$ compound. Figure S2: Rietveld plot obtained from the structural refinement of the (3D+1)-dimensional structure of composite crystal Ca$_{0.83}$CuO$_2$. Figure S3: Synchrotron diffraction patterns collected from 320K to 950K. Figure S4: Rietveld plot obtained from the structural refinement of the Ca-based composite crystal collected at 890K. Table S1: Refined amplitudes of the Fourier expansion associated to each atomic positions in the Ca$_{0.83}$CuO$_2$ (3D+1)-dimensional structure. Table S2: Crystal data for the monoclinic commensurate model of Ca$_5$Cu$_6$O$_{12}$. Table S3. Crystal data for the triclinic commensurate model of Ca$_6$Cu$_7$O$_{14}$ obtained at 890K.

Author Contributions: The synthesis of the ceramic compounds was undertaken by L.R. The synchrotron diffraction experiment has been conducted by L.R., M.M. and M.G.; methodology, M.M.; analysis of the diffraction data L.R.; data treatment of the synchrotron diffraction data, M.M.; writing—original draft preparation, L.R.; writing—review and editing, L.R. and M.G. All authors have read and agreed to the published version of the manuscript.
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