Superconducting Cuprates and Related Oxides. II. Profile Refinement of Neutron Powder Diffraction Data

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Structural data were obtained by profile refinement of neutron diffraction powder patterns of cuprates. Space group $I4/mmm$, No. 139: $La_{1.8}Ba_{0.2}CuO_4$, $a = 3.8008(3)$, $c = 13.3608(8)$ Å, $La_{1.9}Ca_{0.1}CuO_4$, $a = 3.8015(4)$, $c = 13.2176(10)$ Å, $La_{1.8}Ca_{0.2}CuO_4$, $a = 3.8013(4)$, $c = 13.2325(9)$ Å, $La_2Cu_{0.5}Ni_{0.5}O_4$, $a = 3.8512(4)$, $c = 13.0010(12)$ Å. Space group $Abma$, No. 64: $La_2Cu_{0.8}Zn_{0.2}O_4$, $a = 5.4041(4)$, $b = 13.1545(6)$, $c = 5.4564(4)$ Å. Space group $Pmmm$, No. 47: $HoSrBaCu_3O_7$, $a = 3.8460(6)$, $b = 3.8422(7)$, $c = 11.6727(11)$ Å, $NdSrBaCu_3O_7$, $a = 3.8935(6)$, $b = 3.8687(5)$, $c = 11.7074(15)$ Å, $LaSrBaCu_3O_7$, $a = 3.9024(8)$, $b = 3.9067(8)$, $c = 11.7688(19)$ Å, $NdCaBaCu_3O_7$, $a = 3.8944(3)$, $b = 3.8837(4)$, $c = 11.6559(27)$ Å, $LaCaBaCu_3O_7$, $a = 3.9076(9)$, $b = 3.8912(8)$, $c = 11.7127(28)$ Å.

The discovery of superconductivity in the compounds $La_{2-x}Ba_xCuO_4$ and $YBa_2Cu_3O_7$ created an enormous interest in the investigations of cuprates, and hundreds of publications on the preparation and characterization of ternary and quaternary cuprates with potential superconductive properties have now been published. Structural characterizations by X-ray and neutron diffraction analysis have been essential elements of these studies. In this study neutron powder diffraction was combined with profile refinements in an analysis of compounds with structures related to the structure of $La_{2-x}Ba_xCuO_4$ and $YBa_2Cu_3O_7$.

In the compound La_2CuO_4 substitution may take place of the lanthanum as well as of the copper ions with other ions, and in similar ways substitution of yttrium, barium and copper ions may be realized in the compound $YBa_2Cu_3O_7$. The effect of such substitutions on the structures is investigated and reported below.

Experimental

The compounds investigated were made by solid-state synthesis, and the unit cell parameters were determined from X-ray powder patterns as described in Ref. 1. The neutron diffraction powder patterns of the compounds were measured at room temperature in the 2θ range 6–112° in steps of 0.052 88° using $\lambda = 1.076$ Å neutrons and the multi-detector powder diffractometer at DR3, Risø National Laboratory,[2] Denmark. The samples were housed in 8 or 11 mm diameter thin-walled vanadium containers, and the measuring time for a pattern was typically 12 h. The models for the structures were refined by the profile refinement method[3] using the programs EDINP[4] and DBW3.2S.[5]

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The latter can simultaneously refine models of up to eight phases contributing to the powder pattern. The atomic scattering cross-sections for neutrons were taken from Ref. 6.

The peak profile used in the profile refinements was a convolution of a Lorentzian and a Gaussian peak, which gives a peak profile which is symmetrical around the peak position 2θ. The width of the Gaussian varied as $(U \tan^2 \theta + V \tan \theta + W)^{1/2}$, and the width of the Lorentzian varied as $T/\cos \theta$. However, the experimental peak shape, especially in the low 2θ range of the pattern, is not symmetrical around the peak position, and this thus gives a misfit that contributes to the relatively high R-values. The asymmetry of the peak shape is caused by the vertical divergences of the incident and scattered beams, which give rise to a low-angle tail for $2\theta < 90°$ and a high-angle tail for $2\theta > 90°$.[2,7,8] The asymmetry is most pronounced for low-angle reflections with $2\theta < 30°$, where the natural peak width is small. For $2\theta > 150°$ the asymmetry can be neglected, because the natural peak width is large. The present version of EDINP does not model an asymmetric peak, and this causes the R-factors to be higher than are normal in profile refinements. However, the structural parameters are almost unaffected by the misfit of the profile.

The R-values quoted below are: $R = 100\Sigma |y_{obs} - |y_{calc}|| / \Sigma |y_{obs}|$, $R_F = 100\Sigma ||F_{obs}| - |F_{calc}|| / \Sigma |F_{obs}|$ and $R_{expected} = 100 [(N-P)/\Sigma w y_{obs}^2]^{1/2}$. $R_{ALLHKL} = 100\Sigma |y_{obs} - |y'_{calc}|| / \Sigma |y_{obs}|$ is calculated with the program ALLHKL,[9] that extracts structure factors from a powder pattern in a least-squares profile fit, where the preconditions for the calculation are the unit cell and space group of the structure of the compound. y'_{calc} is calculated differently from y_{calc}, which needs a model for the structure. A comparison of the R-values with the R_{ALLHKL}-values gives an idea of how well the profile calcu-

lated with the model of the structure fits the observed profile in a least-squares calculation. The same profile functions are used in the two least-squares fits, with EDINP, yielding R-values, and ALLHKL, yielding R_{ALLHKL}-values. These latter are the lowest reliability values that can be obtained in a least-squares profile fit to the observed powder pattern, when the same profile func-

tion is used in the calculation of R and R_{ALLHKL}, and the pattern has no anisotropic line broadening.

Results and discussion

Structures related to the K_2NiF_4 structure. The structure of $La_{1.85}Ba_{0.15}CuO_4$ was investigated by Jorgensen et al.[10] by neutron powder diffractometry and the refined parameters in space group $I4/mmm$ were: $a = 3.7873(1)$, $c = 13.2883(3)$ Å, $z_{La} = 0.36063(9)$, $z_{O2} = 0.1828(2)$. The temperature factor parameters for the atoms were not listed, but from the figure in Ref. 10 showing the model of the structure it is clear that the temperature factors for the oxygen atom O2 are significantly larger than for the oxygen atom O1.

The results of the profile refinement of the structure of $La_{1.8}Ba_{0.2}CuO_4$ are listed in Table 1, and Fig. 1 shows a plot of observed and calculated profiles and a difference plot.

The investigation of this structure was made to get an idea of the quality of the powder patterns measured at the neutron powder diffractometer at DR3, and to investigate how well the results obtained by a profile refinement of the model of the structure would agree with the results from a known structure, also determined by neutron powder diffractometry. The positional parameters arrived at in this investigation are less accurate than the values reported in Ref. 10, where the standard deviations are approximately one third of the standard deviations found by us. This is presumably due to the more extensive data set measured in Ref. 10, where a larger portion of the reciprocal space was covered.

The models for the structures of $La_{1.9}Ca_{0.1}CuO_4$, $La_{1.8}Ca_{0.2}CuO_4$ and $La_2Cu_{0.5}Ni_{0.5}O_4$ were also refined using space group $I4/mmm$, and the results are listed in Table 1.

The compound $La_2Cu_{0.8}Zn_{0.2}O_4$ has an orthorhombic structure like La_2CuO_4,[11] and the results of the refinement of the model of the structure in space group *Abma* (a non-standard setting of No. 64), are listed in Table 2.

Table 1. Atomic coordinates of compounds with the K_2NiF_4 structure, space group *I4/mmm*, No. 139. Unit cell parameters in square brackets are from powder X-ray diffraction,[1] where a position-sensitive detector was used, and this gives higher standard deviations for the unit cell parameters than the neutron powder diffraction data.

Atom	x/a	y/b	z/c	B/Å²
La₁.₈Ba₀.₂CuO₄				
La, Ba	0	0	0.3591(3)	0.5(1)
Cu	0	0	0	0.4(1)
O1	0	1/2	0	0.5(1)
O2	0	0	0.1798(6)	1.3(1)

$a = 3.8008(3)$	$U = 0.569(14)$	$R = 12.9\%$
[3.794(4)]	$V = -0.604(4)$	$R_F = 13.1\%$
$c = 13.3608(8)$	$W = 0.246(2)$	$R_{expected} = 6.6\%$
[13.349(11)]	$T = 0.060(6)$	$R_{ALLHKL} = 10.6\%$
zero = 0.056(3)		

Atom	x/a	y/b	z/c	B/Å²
La₁.₉Ca₀.₁CuO₄				
La, Ca	0	0	0.3565(3)	0.5(1)
Cu	0	0	0	0.1(1)
O1	0	1/2	0	0.9(1)
O2	0	0	0.1844(5)	1.5(1)

$a = 3.8015(4)$	$U = 0.653(14)$	$R = 11.1\%$
[3.799(2)]	$V = -0.673(5)$	$R_F = 14.6\%$
$c = 13.2176(10)$	$W = 0.261(1)$	$R_{expected} = 5.7\%$
[13.223(6)]	$T = 0.055(6)$	$R_{ALLHKL} = 9.9\%$
zero = 0.087(3)		

Atom	x/a	y/b	z/c	B/Å²
La₁.₈Ca₀.₂CuO₄				
La, Ca	0	0	0.3595(3)	0.8(1)
Cu	0	0	0	0.3(1)
O1	0	1/2	0	0.6(1)
O2	0	0	0.1831(7)	1.4(1)

$a = 3.8013(4)$	$U = 0.568(13)$	$R = 11.0\%$
[3.798(1)]	$V = -0.695(5)$	$R_F = 11.2\%$
$c = 13.2325(9)$	$W = 0.260(2)$	$R_{expected} = 6.2\%$
[13.237(4)]	$T = 0.089(5)$	$R_{ALLHKL} = 9.9\%$
zero = -0.054(3)		

Atom	x/a	y/b	z/c	B/Å²
La₂Cu₀.₅Ni₀.₅O₄				
La	0	0	0.3598(3)	0.4(1)
Cu, Ni	0	0	0	0.4(1)
O1	0	1/2	0	0.3(1)
O2	0	0	0.1794(7)	2.2(1)

$a = 3.8512(4)$	$U = 0.651(2)$	$R = 11.9\%$
[3.843(1)]	$V = -0.689(4)$	$R_F = 14.8\%$
$c = 13.0010(12)$	$W = 0.252(2)$	$R_{expected} = 5.2\%$
[12.985(5)]	$T = 0.086(5)$	$R_{ALLHKL} = 9.8\%$
zero = -0.064(3)		

Table 2. Atomic coordinates of a compound with the La_2CuO_4 structure, space group *Abma*, No. 64. Unit cell parameters in square brackets are from powder X-ray diffraction.[1]

Atom	x/a	y/b	z/c	B/Å²
La₂Cu₀.₈Zn₀.₂O₄				
La	-0.0048(29)	0	0.3591(3)	0.5(1)
Cu, Zn	0	0	0	0.2(1)
O1	1/4	1/4	0.0105(17)	0.3(1)
O2	-0.0309(22)	0	0.1838(7)	1.5(3)

$a = 5.4041(4)$	$U = 1.077(11)$	$R = 9.8\%$
[5.403(3)]	$V = -1.170(3)$	$R_F = 17.4\%$
$b = 13.1545(6)$	$W = 0.397(2)$	$R_{expected} = 6.0\%$
[13.143(5)]	$T = 0.027(4)$	$R_{ALLHKL} = 7.2\%$
$c = 5.4564(4)$		
[5.459(3)]		
zero = 0.151(1)		

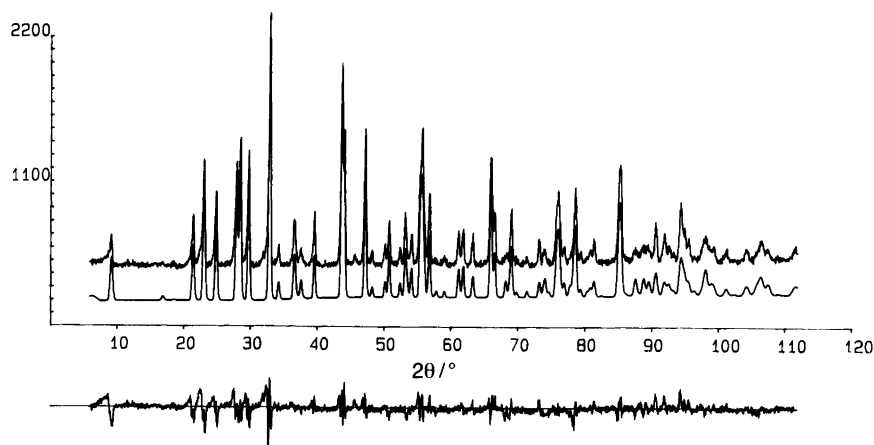*Fig. 1.* Observed and calculated neutron diffraction powder pattern of $La_{1.8}Ba_{0.2}CuO_4$. Difference plot below.

It is characteristic of all the investigated structures related to the K_2NiF_4 structure (Tables 1 and 2), that the oxygen atom O2 has temperature factors that are significantly larger than for those of the oxygen atom O1. As mentioned, this was also the case for the structure of $La_{1.85}Ba_{0.15}CuO_4$.[10]

Structures related to the $YBa_2Cu_3O_7$ structure. Substitution of the metal ions in $YBa_2Cu_3O_7$ by other ions has been studied previously, and examples of compounds thus obtained are $LaCaBaCu_3O_{7-x}$,[12-14] $NdCaBaCu_3O_{7-x}$[14] and $LaSrBaCu_3O_{7-x}$.[14] The structures were investigated[14] by profile refinement of X-ray powder diffraction data, and the chemical formulae found for the compounds were $(LnAe_{x'}Ba)_{3/2-x}Cu_3O_{7-x}$ for the following orthorhombic compounds: $La_{1.23}Ca_{0.54}Ba_{1.23}Cu_3O_{7-x}$ [$a = 3.8722(8)$, $b = 3.8703(8)$, $c = 11.6448(8)$ Å], $Nd_{1.26}Ca_{0.48}Ba_{1.26}Cu_3O_{7-x}$ [$a = 3.875(2)$, $b = 3.874(2)$, $c = 11.6415(8)$ Å], $La_{1.14}Sr_{0.72}Ba_{1.14}Cu_3O_{7-x}$ [$a = 3.8895(7)$, $b = 3.8876(7)$, $c = 11.7212(5)$ Å]. The samples contained impurities of Ca_2CuO_3 and $SrCuO_2$.[14] The Ca^{2+} and Sr^{2+} ions were found to enter not only at the Ba^{2+} ion sites, but also at the La^{3+}/Nd^{3+} site. The occupancy of Ca^{2+} or Sr^{2+} ions at the La^{3+}/Nd^{3+} sites was found to correlate with their ionic radii, so that the Sr^{2+} ions enter at the Ba^{2+} sites in preference to the La^{3+} sites in $La_{1.14}Sr_{0.72}Ba_{1.14}Cu_3O_{7-x}$, and the Ca^{2+} ions enter at the La^{3+} sites in preference to the Ba^{2+} sites in $La_{1.23}Ca_{0.54}Ba_{1.23}Cu_3O_{7-x}$.[14]

The refinements of the neutron diffraction powder patterns of $HoSrBaCu_3O_7$, $NdSrBaCu_3O_7$, $LaSrBaCu_3O_7$, $NdCaBaCu_3O_7$ and $LaCaBaCu_3O_7$ were performed in the following way. The occupancies of the metal atom sites (excluding the copper atom sites) and the sites for the oxygen atoms O4 and O5 were first refined with the temperature factor parameters fixed at 0.55 for the four metal atoms and for the oxygen atoms O2 and O3, and at 1.00 for the oxygen atoms O1, O4 and O5. These refinements could not give a clear indication of the type of substitution of metal atoms reported in Ref. 14, and in the following refinements average scattering lengths for 50 % Ca, 50 % Ba or 50 % Sr, 50 % Ba in site 2*t* were used. The refine-

ment of the occupancies of the oxygen atoms O4 and O5 also gave a somewhat unclear indication of the occupancies of these two sites, as the refinements oscillated between occupancy of O4 greater than occupancy of O5, and occupancy of O4 less than occupancy of O5. However, it was clear that the oxygen content in $HoSrBaCu_3O_7$ was lower than in the other compounds. A possible explanation for this is that the other compounds were annealed in oxygen, whereas this was not the case for $HoSrBaCu_3O_7$. From these refinements of the occupancies, the compositions of the compounds were estimated, as listed in Table 3, and in further refinements the occupancies of the oxygen atoms O4 and O5 were given fixed values.

The programs EDINP[4] and DBW3.2S[5] were used in the refinements, and the results obtained are listed in Table 3.

Conclusion

Of the samples investigated by neutron powder diffraction, $LaCaBaCu_3O_7$ and $NdCaBaCu_3O_7$ showed a content of Ca_2CuO_3 as an impurity. Correction for the scattering contribution from this impurity was made in the profile refinements by the use of the program DBW3.2S using contributions from two phases to the diffraction pattern. The other samples did not contain impurities to a level where corrections were necessary. The compound Ca_2CuO_3 is apparently formed readily in solid-state reactions in preference to the quaternary oxides $LaCaBaCu_3O_7$ and $NdCaBaCu_3O_7$.

It is often difficult to determine the composition of a solid by the use of its neutron diffraction powder pattern and model calculations of the structure of the solid where the occupancy of selected atoms or their scattering lengths are refined. For this reason the nominal compositions of the compounds were assumed in the model calculations, and substitution of atoms were assumed only to take place at one crystallographic site for each compound (Tables 1-3). This assumption gave acceptable results for the refinements of the models, but is not in agreement with the model for the $YBa_2Cu_3O_7$-type structures reported in Ref. 14.

Table 3. Atomic coordinates of compounds with the $YBa_2Cu_3O_7$-type structure, space group *Pmmm*, No. 47. Unit cell parameters in square brackets are from powder X-ray diffraction.[1]

Atom	Occupancy	x/a	y/b	z/c	B/Å²

HoSrBaCu₃O₇ not annealed in oxygen. Composition from refinement: $HoSrBaCu_3O_{6.2(1)}$

Atom	Occupancy	x/a	y/b	z/c	B/Å²
Ho	1	1/2	1/2	1/2	0.55
Sr,Ba	2	1/2	1/2	0.1951(8)	0.55
Cu1	1	0	0	0	0.55
Cu2	2	0	0	0.3550(8)	0.55
O1	2	0	0	0.1566(11)	1.00
O2	2	1/2	0	0.3691(14)	0.55
O3	2	0	1/2	0.3749(8)	0.55
O4	0.13(6)	0	1/2	0	1.00
O5	0.11(6)	1/2	0	0	1.00

a = 3.8460(6) [3.851(1)]
b = 3.8422(7) [3.851(1)]
c = 11.6727(11) [11.662(3)]
zero = 0.092(1)

U = 0.621(14)
V = −0.559(5)
W = 0.203(2)
T = 0.052(4)

R = 9.0 %
R_F = 13.4 %
$R_{expected}$ = 5.2 %
R_{ALLHKL} = 6.0 %

NdSrBaCu₃O₇ annealed in oxygen at 950 °C. Composition from refinement: $NdSrBaCu_3O_{6.8(1)}$

Atom	Occupancy	x/a	y/b	z/c	B/Å²
Nd	1	1/2	1/2	1/2	0.55
Sr,Ba	2	1/2	1/2	0.1786(11)	0.55
Cu1	1	0	0	0	0.55
Cu2	2	0	0	0.3528(7)	0.55
O1	2	0	0	0.1668(15)	1.00
O2	2	1/2	0	0.3610(31)	0.55
O3	2	0	1/2	0.3729(27)	0.55
O4	0.86(12)	0	1/2	0	1.00
O5	0.0(1)	1/2	0	0	1.00

a = 3.8935(6) [3.877(2)]
b = 3.8687(5) [3.877(2)]
c = 11.7074(15) [11.675(6)]
zero = 0.002(1)

U = 0.644(13)
V = −0.590(6)
W = 0.197(2)
T = 0.098(4)

R = 11.2 %
R_F = 12.3 %
$R_{expected}$ = 7.8 %
R_{ALLHKL} = 8.2 %

LaSrBaCu₃O₇ annealed in oxygen at 950 and 400 °C. Composition from refinement: $LaSrBaCu_3O_{6.8(1)}$

Atom	Occupancy	x/a	y/b	z/c	B/Å²
La	1	1/2	1/2	1/2	0.55
Sr,Ba	2	1/2	1/2	0.1813(17)	0.55
Cu1	1	0	0	0	0.55
Cu2	2	0	0	0.3433(13)	0.55
O1	2	0	0	0.1488(29)	1.00
O2	2	1/2	0	0.3733(18)	0.55
O3	2	0	1/2	0.3541(10)	0.55
O4	0.80(10)	0	1/2	0	1.00
O5	0.0(1)	1/2	0	0	1.00

a = 3.9130(8) [3.900(3)]
b = 3.9023(8) [3.900(3)]
c = 11.7688(19) [11.773(12)]
zero = 0.004(1)

U = 0.621(14)
V = −0.637(15)
W = 0.230(2)
T = 0.113(5)

R = 8.7 %
R_F = 22.9 %
$R_{expected}$ = 4.7 %
R_{ALLHKL} = 6.0 %

contd.

Table 3 (contd.)

Atom	Occupancy	x/a	y/b	z/c	B/Å²

NdCaBaCu₃O₇ annealed in oxygen at 950 and 400 °C. Composition from refinement: $NdCaBaCu_3O_{6.4(2)}$. Program DBW 3.2S used

Atom	Occupancy	x/a	y/b	z/c	B/Å²
Nd	1	1/2	1/2	1/2	0.55
Ca, Ba	2	1/2	1/2	0.1811(12)	0.55
Cu1	1	0	0	0	0.55
Cu2	2	0	0	0.3537(11)	0.55
O1	2	0	0	0.1586(22)	1.00
O2	2	1/2	0	0.3691(18)	0.55
O3	2	0	1/2	0.3607(19)	0.55
O4	0.15(7)	0	1/2	0	1.00
O5	0.14(7)	1/2	0	0	1.00

a = 3.8944(3) [3.882(2)]
b = 3.8837(4) [3.882(1)]
c = 11.6559(27) [11.663(5)]
zero = 0.053(7)

U = 0.751(31)
V = −0.652(16)
W = 0.333(7)

R = 9.4 %
$R_{expected}$ = 6.4 %
R_{ALLHKL} = 6.9 %

LaCaBaCu₃O₇ annealed in oxygen at 950 and 400 °C. Composition from refinement: $LaCaBaCu_3O_{6.4(1)}$. Program DBW 3.2S used

Atom	Occupancy	x/a	y/b	z/c	B/Å²
La	1	1/2	1/2	1/2	0.55
Ca, Ba	2	1/2	1/2	0.1806(10)	0.55
Cu1	1	0	0	0	0.55
Cu2	2	0	0	0.3508(10)	0.55
O1	2	0	0	0.1565(20)	1.00
O2	2	1/2	0	0.3654(18)	0.55
O3	2	0	1/2	0.3670(20)	0.55
O4	0.38(7)	0	1/2	0	1.00
O5	0.0(1)	1/2	0	0	1.00

a = 3.9076(9) [3.907(2)]
b = 3.8912(8) [3.907(2)]
c = 11.7127(28) [11.687(4)]
zero = 0.059(5)

U = 0.671(30)
V = −0.601(15)
W = 0.292(5)

R = 11.1 %
$R_{expected}$ = 5.1 %
R_{ALLHKL} = 6.9 %

The substitution of lanthanum ions in La_2CuO_4 with Ca^{2+} ions, which are smaller than La^{3+} ions, and with Sr^{2+} and Ba^{2+} ions, which are larger than La^{3+} ions, results in a small contraction in the *ab*-plane, in an expansion of the *c*-axis, and in the tetragonal symmetry of the crystal.

The substitution of copper ions in La_2CuO_4 with Ni^{2+} ions, which are smaller than Cu^{2+} ions, results in an expansion in the *ab*-plane and a contraction in the direction of the *c*-axis. In addition, the orthorhombic structure changes to tetragonal symmetry for $La_2Cu_{0.5}Ni_{0.5}O_4$.

Substitution with Zn^{2+} ions, which are larger than Cu^{2+} ions, results in an expansion in the *ab*-plane and a contraction in the direction of the *c*-axis. The orthorhombic structure of La_2CuO_4 is conserved for the solid solution up to at least the composition $La_2Cu_{0.8}Zn_{0.2}O_4$.

In the structures of the $YBa_2Cu_3O_7$ type it is observed that the substitution of Ba^{2+} ions with Sr^{2+} or Ca^{2+} ions results in a reduction of the volume of the unit cell originating mostly from a significant contraction of the c-axis.

It is interesting to note that the substitution of La^{3+} in La_2CuO_4 with Ca^{2+}, Sr^{2+} and Ba^{2+} results in expansion of the c-axis of the unit cell compared to that of La_2CuO_4, and the compounds have higher values for the transition temperatures to superconductivity than La_2CuO_4. The substitution of the Ba^{2+} ions in the $YBa_2Cu_3O_7$-type structures with Ca^{2+} and Sr^{2+} ions results in a contraction of the c-axis, and the substituted compounds have lower transition temperatures to superconductivity than the non-substituted compounds.

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