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STRUCTURES OF SUPERCONDUCTING $BA_2YCU_3O_{7-\partial}$ AND SEMICONDUCTING $BA_2YCU_3O_6$ BETWEEN 25°C AND 750°C.

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The structure and copper valence states of the 100K superconductor, $Ba_2YCu_3O_7$ have recently been determined by neutron powder diffraction between 5K and 300K[1], and at room temperature[2]. This 'oxygen deficient orthorhombic perovskite structure', now independently confirmed[3,4], is well ordered and stochiometric, and contains one Cu^{+++} and two Cu^{++} atoms distributed over two square planar oxygen co-ordinated sites. In the a-b plane CuO_4 squares are linked by their oxygen corners to form infinite sheets, while along the b-axis CuO_4 squares form infinite chains on the second Cu-site. In this paper we show that when $Ba_2YCu_3O_7$ is heated above room temperature, it progressively loses all oxygen from the O4 sites on the b-axis chains, while the remaining oxygen sites remain fully occupied. Near 700°C it becomes tetragonal[5], with the P4/mmm $Ba_2YCu_3O_6$ structure obtained by X-ray diffraction at room temperature[6]. This material is well ordered, stochiometric and stable when cooled under vacuum. The valence of Cu2 in the a-b sheets remains close to 2, while that of Cu1 in the b-axis chains falls to near 1. The valence of copper in these chains can perhaps fluctuate, since the vibration of O4 out of the chain, which we observed even at 5K[1], implies a reduction of the valence charge on this copper site. We have observed similar large amplitude oxygen vibration at low temperature in La_2CuO_4.

THE $BA_2YCU_3O_7$ MATERIAL was a fresh sample, prepared by the same method described in our earlier paper[1]. All neutron diffraction measurements were performed on the new high resolution powder diffractometer D2B at the ILL Grenoble[7], but since the line widths were determined by the sample rather than the diffractometer, we operated in the high flux mode with a resolution similar to that obtained on D1A for the earlier measurements. The neutron wavelength was 1.5946 Å, and a complete diffraction pattern covering 160° was obtained each 12 minutes. The thermal equilibrium of the sample could thus be monitored. To ensure good statistics, 10 seperate scans were averaged to obtain the data at 25°C, 250°C and 700°C. From 2 to 6 scans were averaged at the other temperatures.

Rietveld profile refinement of the data was performed as in the earlier work[1]. Nothing was assumed about the changes in either the unit cell or the oxygen occupancies. Starting with the ambient temperature structure, we refined the data at progressively higher temperature, always in the orthorhombic space group Pmmm. The lattice dimensions and the occupancies of all the oxygen sites were allowed to vary as free and independent parameters. In this way, the large changes of these parameters with temperature could be followed.

The first measurements, up to 250°C, were performed in a molybdenum furnace in air, with an empty furnace run to subtract the molybdenum lines from the diffraction pattern. We first confirmed the $Ba_2YCu_3O_7$ structure at ambient temperature, and verified that the sample was indeed a single phase. A good fit to the data was obtained (column 25°C(1) in table1a) with parameters almost identical to those obtained earlier for a different sample on a different diffractometer[1]. The diffraction pattern was obtained with about the same resolution, but to higher $\sin(\theta/\lambda)$ (figure 1a), and there are no extraneous lines.

The measurement at 250°C in air shows that no oxygen is lost at this temperature since all oxygen occupation numbers refine to almost unity. In fact the sample appears to have picked up a little oxygen at 250°C, since the O4 occupancy (along the b-axis CuO_4 chains) is now 0.99 instead of the original 0.93, which was lower than the value obtained for the earlier material[1].

The sample was then heated to 500°C in air, but no data was obtained under these conditions because the furnace element was rapidly oxidised. Refinement of the structure after rapid cooling in air from 500°C revealed that some oxygen has already been lost from the O4 position: the occupation of this position has fallen from 1.0 to 0.77 (column 25°C(2) in table 1a). Disorder of O4 perpendicular to the b-axis chains appears to have been quenched in, since the O4 B11-factor for this 25°C(2) run is much larger than for the original 25°C(1) scan.

The sample was then reheated to 500°C in a vacuum furnace. Gas pressure measurements showed that additional oxygen was initially lost, but stability was rapidly obtained. Refinement of the diffraction data showed that all oxygen occupancies are still close to unity, with the exception of O4, where the occupation has fallen to 0.59 (column 500°C of table 1a). Already at this temperature, the diffraction pattern shows the presence of line broadening, indicating that coherent regions of the O_7 phase in the the sample are small. Above 500°C, regions of the sample may already be tetragonal. It is then more difficult

Table 1a. Lattice dimensions a,b,c and atomic co-ordinate and temperature factor parameters for orthorhombic Pmmm $Ba_2YCu_3O_7$. The occupation numbers n for the oxygen sites remain near 1 at all temperatures, except for O4, which departs on heating.

		25°C(1)	250°C	25°C(2)	500°C	600°C
	a	3.8193(2)	3.8300(1)	3.8274(2)	3.8577(3)	3.8818(5)
	b	3.8852(2)	3.8950(1)	3.8904(2)	3.9061(4)	3.8972(5)
	c	11.6873(7)	11.7374(5)	11.7177(6)	11.8385(12)	11.8942(12)
Ba	z	0.1839(5)	0.1848 (3)	0.1863(3)	0.1897(5)	0.1910(6)
	B	0.61(10)	0.73 (5)	0.67 (7)	1.69 (13)	2.04 (16)
Y	B	0.69(10)	1.46 (6)	0.94 (7)	1.13 (11)	1.51 (13)
Cu1	B	0.51(10)	1.43 (6)	1.20 (7)	1.69 (13)	1.89 (14)
Cu2	z	0.3545(3)	0.3553(2)	0.3576(2)	0.3592(4)	0.3630(5)
	B	0.34(5)	0.91 (4)	0.78 (5)	1.21 (8)	1.65 (10)
O1	z	0.1575(5)	0.1575(3)	0.1563(5)	0.1539(6)	0.1492(7)
	n	0.97(2)	0.95(2)	1.03(2)	0.99(2)	0.98(2)
	B	0.66(14)	1.24 (7)	1.44 (10)	2.13 (18)	3.0 (24)
O2	z	0.3783(5)	0.3773(3)	0.3796(3)	0.3824(7)	0.3823(8)
	n	0.97(2)	1.01(1)	1.01(1)	1.00(2)	0.95(4)
	B	0.63(13)	1.22 (7)	1.02 (8)	1.65 (18)	0.27 (20)
O3	z	0.3775(5)	0.3778(3)	0.3778(4)	0.3759(7)	0.3703(11)
	n	0.99(2)	0.98(1)	0.97(1)	0.95(2)	1.00(4)
	B	0.41(13)	1.13 (7)	0.87 (10)	0.75 (16)	2.35 (30)
O4	n	0.93(4)	0.99(2)	0.77(2)	0.59(3)	0.37(4)
	B11	2.7 (5)	4.1 (3)	7.7 (7)	12.6 (2.2)	51.0 (2.8)
	B22	0.4 (4)	0.4 (2)	0.8 (3)	1.7 (9)	10.6 (4.8)
	B33	1.2 (5)	3.4 (3)	1.0 (4)	2.6 (1.3)	-1.9 (1.7)
Rn		7.9	9.5	8.8	9.4	15.4

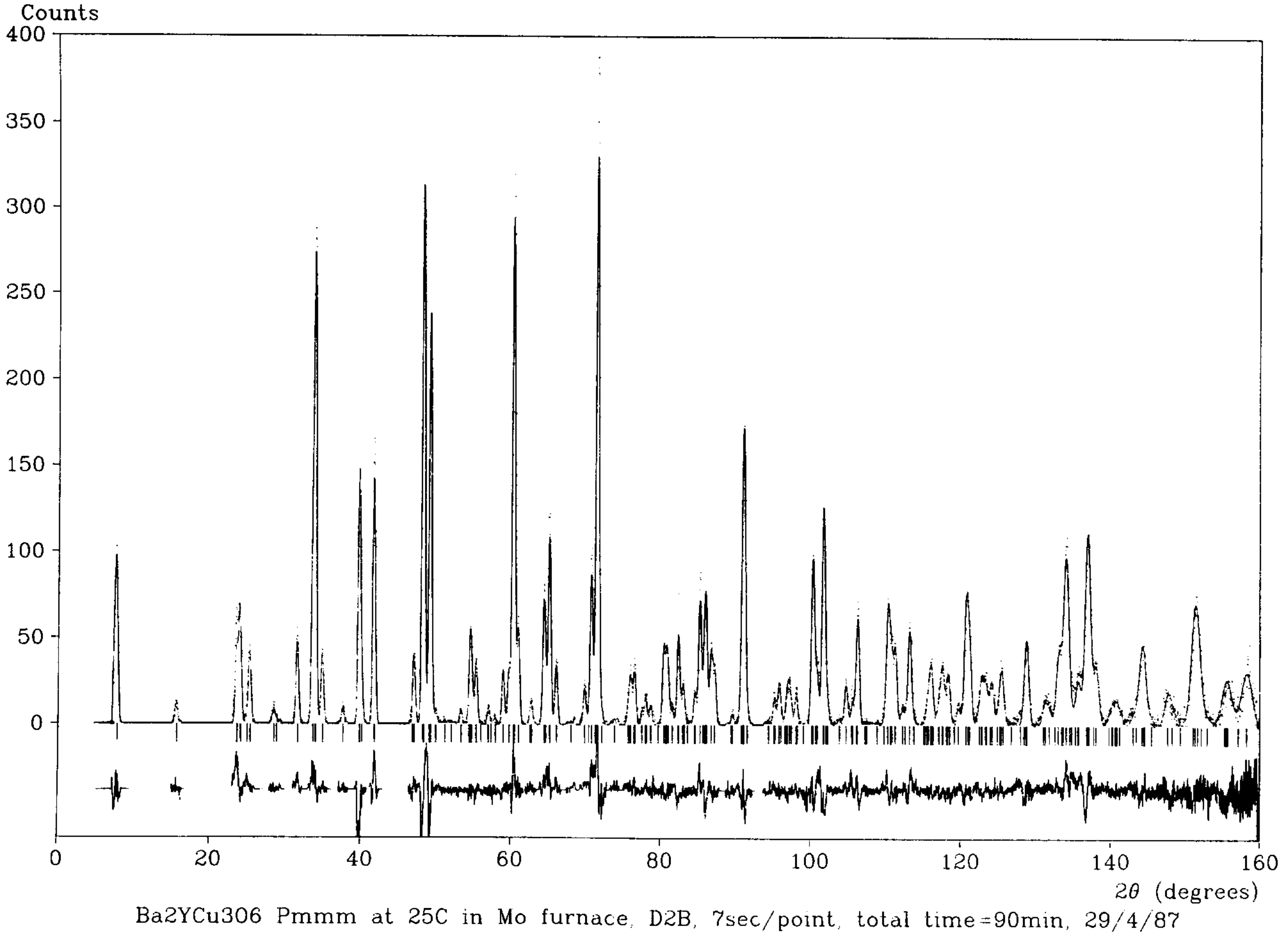


Fig.1. Observed and calculated neutron powder diffraction patterns for
(a) Orthorhombic Ba$_2$YCu$_3$O$_7$ at 25°C before heating.

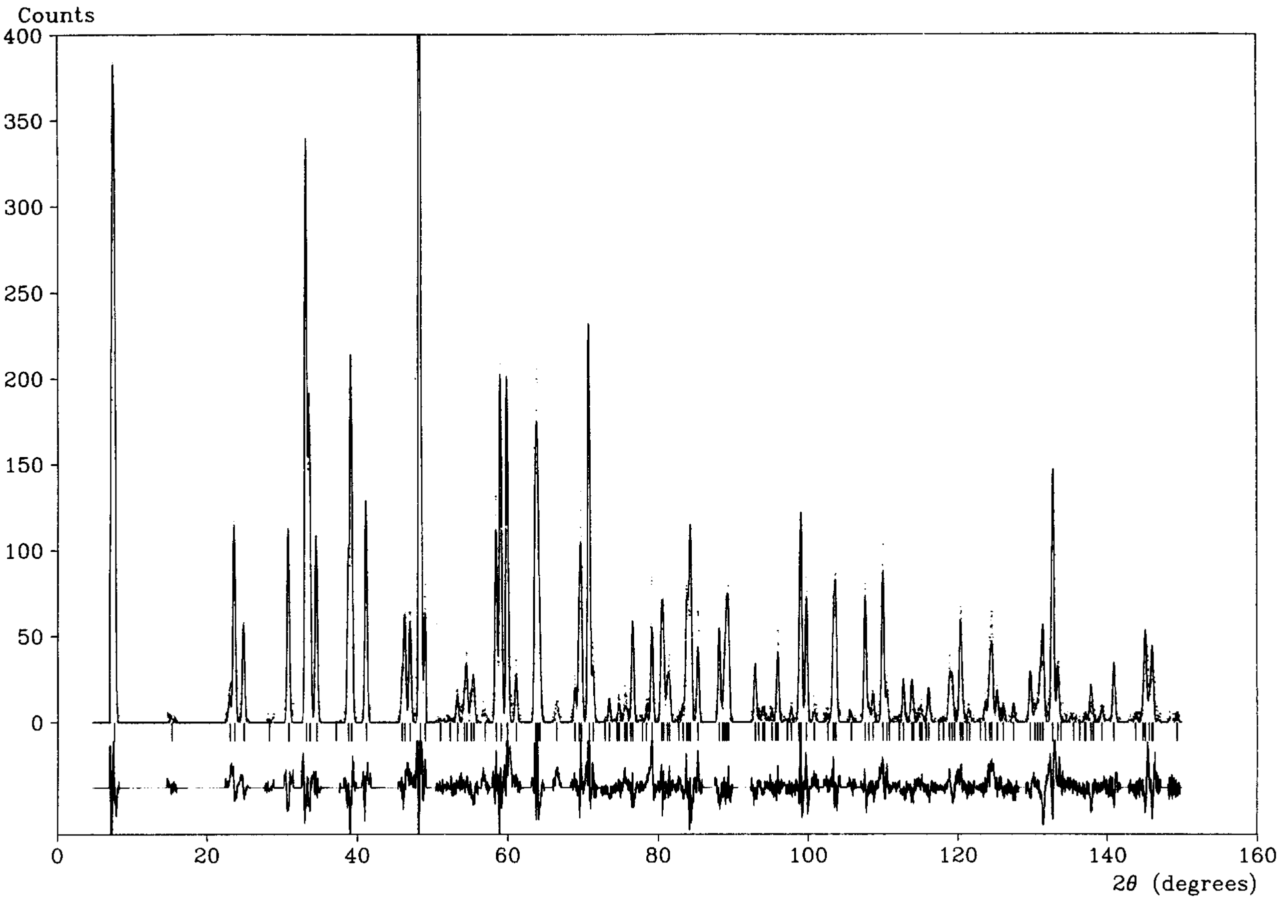
to describe the line profile, resulting in poorer fits to the data. For the orthorhombic phase, the a- and b- axes have started to converge.

At 600°C, the a- and b-axes have become nearly equal. The O4 occupation has fallen to 0.37, while the remaining oxygen positions remain fully occupied. Note that thermal disorder of O4, which is always of relatively large amplitude perpendicular to the Cu-O bond, increases rapidly with temperature: at 600°C O4 is no longer really within the chain, but disordered towards the y-axis channels on either side. These channels would of course be occupied in the perovskite structure by additional columns of oxygen, and we might expect therefore, ionic oxygen conduction along the b-axis.

The data at 700°C was also refined in the orthorhombic cell, but the a- and b-axes become identical, with the occupancy of O4 falling to zero within experimental error. Further refinement was therefore performed in the tetragonal space group P4/mmm (table 1b). At 700°C, the diffraction pattern shows a pure single tetragonal phase, which refines to give a well ordered P4/mmm Ba$_2$YCu$_3$O$_6$ structure.

On increasing the temperature further, the tetragonal phase diffraction pattern remains unchanged, but weak additional lines appear at 750°C, indicating decomposition. When the sample was later examined visually, a small amount of reddish-brown material was observed on its surface.

Finally, the sample was cooled under vacuum, with diffraction data collected at approximately 600°C, 500°C, 250°C and 100°C. The pattern remains unchanged on cooling, except that of course the tetragonal cell dimens-



Ba2YCu3O6 P4/mmm at 750C in vacuum on D2B, 7sec/point, total time=75min, 29/4/87

Fig.1. (b) Tetragonal $Ba_2YCu_3O_6$ at 750°C.
At 25°C the pattern is very similar.

ions decrease. A (necessarily disordered) atom position O4 was included, and the occupancies of all oxygen atoms refined systematically. O4 was removed for the final refinements, since there was always effectively zero occupation of this position in tetragonal $Ba_2YCu_3O_6$. On cooling, the structure converges towards that obtained for the Ba-excess stabilised room temperature phase[6] $Ba_{2.1}Y_{0.9}Cu_3O_6$.

In this tetragonal phase, table 1b shows that the O2=O3 oxygen sites within the CuO_4 sheets, as well as the out-of-sheet O1 site, remain fully occupied with normal vibrational amplitudes. Only O1 has a somewhat larger B-factor. $Ba_2YCu_3O_6$ is then a well ordered, stochiometric single phase containing two Cu^{++} and one Cu^{+} ions. High resolution electron micrographs of this phase (figure 2) show that, as in $Ba_2YCu_3O_7$[8], the material is ordered over large distances with no extrinsic Ba or Y planes.

Table 2 lists the bond lengths and valence charges for a) the orthorhombic phase up to 600°C, and b) the tetragonal phase from 750°C and cooling. The copper valence charges Z have been calculated as before[1] using the Zachariasen formula[9], confirming our earlier result that the Cu^{+++} is distributed between the two copper sites in $Ba_2YCu_3O_7$. The Zachariasen parameter D1=1.74 Å at 25°C[1], has been corrected for thermal expansion of the cell volume. The calculation for Cu1 within the chain takes account of the fact that the O4 site is not fully occupied at high temperature, but the mean Cu-O4 distance has not been corrected for the large thermal disorder of this ion. In $Ba_2YCu_3O_6$ the valence on Cu2 remains close to 2, while the valence of Cu1 falls to near 1, with its oxygen co-ordination changing from 4 to 2 (table 2b). The corresponding Zachariasen parameter D1=1.65 Å for Cu^{+} has been calculated from the structure of Cu_2O[12].

These valence charge values have been confirmed using the alternative Brown-Shannon[10] formula used in

Table 1b. Lattice dimensions a,b,c and atomic co-ordinate and temperature factor pameters for tetra gonal P4/mmm $Ba_2YCu_3O_6$. The occupations n show no additional oxygen loss after all oxygen at site O4 has left.

		750°C	700°C	600°C	500°C	250°C	100°C
	a=b	3.8920(1)	3.8908(1)	3.8801(2)	3.8728(1)	3.8690(1)	3.8665(1)
	c	11.9909(3)	11.9735(5)	11.9391(6)	11.9105(5)	11.8934(4)	11.8822(4)
Ba	z	0.1944(3)	0.1934(4)	0.1948(4)	0.1960(4)	0.1950(4)	0.1937(3)
	B	2.25(6)	1.30 (8)	1.34 (10)	0.52 (8)	1.26 (8)	1.20 (7)
Y	B	1.69(5)	1.30 (8)	1.05 (9)	1.43 (1)	0.89 (7)	0.65 (6)
Cu1	B	3.13(7)	2.73 (10)	2.03 (11)	2.57 (11)	1.64 (8)	1.51 (7)
Cu2	z	0.3613(2)	0.3620(3)	0.3608(3)	0.3621(3)	0.3616(2)	0.3619(2)
	B	1.75(4)	1.29 (6)	1.11 (6)	1.28 (6)	0.75 (5)	0.93 (4)
O1	z	0.1501(3)	0.1498(5)	0.1494(5)	0.1497(6)	0.1506(4)	0.1512(4)
	n	1.00(1)	1.00(1)	0.96(1)	0.96(1)	1.01(1)	1.00(1)
	B	3.74(9)	3.25 (13)	2.35 (14)	2.75 (14)	2.2 (10)	2.30 (10)
O2=O3	z	0.3791(2)	0.3792(2)	0.3778(3)	0.3782(3)	0.3789(2)	0.3788(2)
	n	0.99(1)	0.98(1)	0.97(2)	0.95(2)	0.99(1)	0.98(1)
	B	2.01(4)	1.56 (6)	0.88 (6)	0.94 (6)	0.98 (5)	0.96 (4)
R_n		10.5	15.9	16.8	19.5	11.8	12.9

Fig. 2. High resolution 200kV electron diffraction image at Scherzer defocus of $Ba_2YCu_3O_6$ projected down the 100 axis. As for $Ba_2YCu_3O_7$[8], the structure of $Ba_2YCu_3O_6$ is well ordered over large distances. The heavier atoms are darker, and the brightest rows of spots correspond to the empty tunnels on the Cu1 planes. In the optical diffraction pattern (inset) reflections of the type (h,k,3n), corresponding to the basic perovskite subunit, are relatively intense.

reference 4, and the Brown-Altermatt[11] formula . The Zachariasen or Brown-Altermatt formulae have the advantage that parameters B and D1xA, unlike Brown-Shannon's N, vary little between different atom pairs.

The transition reported here between $Ba_2YCu_3O_7$ and $Ba_2YCu_3O_6$ illustrates the instability of the O4 oxygen site, and the resulting ease with which Cu1 along the b-axis chains can accept electrons, its valence changing from 2.5 to near 1. Even at 5K in $Ba_2YCu_3O_7$ we found that O4 was unstable to out-of-chain vibrations[1]. Such large amplitude vibrations occur because of the empty columns on either side of these chains, normally filled by additional oxygen in the perovskite structure. When O4 moves out of the chain, the valence of Cu1 may be reduced, since the size of the Cu1 site is thereby increased, and Cu^{++} is larger than Cu^{+++}. There may be a dynamic coupling between valence fluctations and this transverse vibrational mode.

Our unpublished structural measurements on La_2CuO_4, show that similar vibrations occur for the out-of-plane oxygen, even at 1.5K, though the amplitude is lower than in $Ba_2YCu_3O_7$: this motion eventually results in the orthorhombic to tetragonal phase transition above room temperature.

The displacement of O4 toward the b-axis channels leads us to suppose that the material is an oxygen conductor above about 250°C, and that this mechanism is responsible for changes in oxgen stochiometry which degrade the superconducting properties. The sharpest and highest Tc's appear to occur for materials with full O4 occupancy along the b-axis chains.

Table 2a. Bond lengths for orthorhombic Pmmm $Ba_2YCu_3O_7$. By 700°C the cell is tetragonal P4/mmm, since O4, which begins to disappear between 250°C and 500°C, has been completely removed. At 500°C and 600°C, the sample is not a pure single phase, and the refinement gives only an average structure. The Zachariasen valence Z has been corrected for thermal expansion and partial contribution of O4.

		20°C(1)	250°C	20°C(2)	500°C	600°C
Ba	-O1x4	2.741(1)	2.750(1)	2.751(1)	2.778(1)	2.795(2)
	-O2x2	2.990(6)	2.984(3)	2.986(4)	3.003(7)	2.996(9)
	-O3x2	2.961(7)	2.967(3)	2.949(4)	2.930(7)	2.883(11)
	-O4x2	2.875(5)	2.893(2)	2.903(3)	2.960(4)	2.988(5)
	-Mean	2.862	2.869	2.868	2.890	2.891
Y	-O2x4	2.407(3)	2.422(2)	2.403(2)	2.398(5)	2.399(6)
	-O3x4	2.387(4)	2.392(2)	2.390(3)	2.424(5)	2.480(8)
	-Mean	2.397	2.407	2.397	2.411	2.439
Cu1	-O1x2	1.840(6)	1.849(3)	1.831(4)	1.822(7)	1.775(9)
	-O4x2	1.943(0)	1.947(0)	1.945(0)	1.953(0)	1.949(0)
	-Mean	1.892	1.898	1.888	1.887	1.862
	-Z	2.411(27)	2.477(13)	2.311(19)	2.252(34)	2.313(48)
Cu2	-O1x1	2.303(7)	2.321(4)	2.359(5)	2.430(8)	2.543(11)
	-O2x2	1.930(1)	1.932(1)	1.931(1)	1.949(1)	1.954(1)
	-O3x2	1.961(1)	1.965(1)	1.959(1)	1.963(1)	1.951(1)
	-Mean	2.017	2.023	2.028	2.051	2.071
	-Z	2.225(10)	2.238(8)	2.227(8)	2.330(10)	2.257(10)

Table 2b. Bond lengths for tetragonal P4/mmm $Ba_2YCu_3O_6$. With the loss of oxygen, and the transition from Pmmm $Ba_2YCu_3O_7$ to P4/mmm $Ba_2YCu_3O_6$, the Cu2 valence Z remains near 2, while the Cu1 valence decreases markedly. The Zachariasen Z parameter D1=1.647 for Cu^+ has been estimated from Cu_2O.

		750°C	700°C	600°C	500°C	250°C	100°C
Ba	-O1x4	2.803(1)	2.800(1)	2.797(2)	2.793(2)	2.786(1)	2.780(1)
	-O2x4	2.948(3)	2.955(4)	2.922(4)	2.909(4)	2.920(4)	2.929(3)
	-Mean	2.875	2.878	2.859	2.851	2.853	2.854
Y	-O2x8	2.427(1)	2.424(2)	2.427(2)	2.419(2)	2.412(2)	2.411(1)
Cu1	-O1x2	1.800(4)	1.793(6)	1.784(6)	1.783(7)	1.791(5)	1.797(5)
	-Z(Cu^+)	1.241(16)	1.266(25)	1.285(26)	1.275(30)	1.231(20)	1.200(20)
Cu2	-O1x1	2.532(5)	2.542(6)	2.524(7)	2.530(8)	2.510(6)	2.503(5)
	-O2x4	1.958(0)	1.956(0)	1.951(1)	1.946(1)	1.946(0)	1.944(0)
	-Mean	2.073	2.073	2.065	2.063	2.058	2.056
	-Z(Cu^{++})	2.159(10)	2.156(10)	2.160(8)	2.162(8)	2.154(10)	2.158(10)

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