Structure and Superconductivity in $(Bi_{0.35}Cu_{0.65})Sr_2YCu_2O_7$ and Related Materials

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The recently reported $(Bi/Cu)Sr_2YCu_2O_7$ phase has been studied by time of flight powder neutron diffraction. The proposed 1212 structure has been confirmed and refinements have shown the oxygen in the (Bi/Cu)O layer is displaced by 0.78Å from the ideal (½,½,0) site (P4/mmm space group) along {100}. Bond Valence Sum calculations have suggested oxidation states of Bi^{5+} and Cu^{2+} for the cations in the (Bi/Cu)O layers. The material is non-superconducting and all attempts to induce superconductivity have been unsuccessful. Work on the related material $(Ce/Cu)Sr_2YCu_2O_7$ has shown the ideal Ce content to be 0.5 Ce per formula unit. The introduction of Ba (10%) onto the Sr site dramatically increases phase stability and also induces superconductivity (62K).

Introduction

The discovery of high T_c superconductivity in the system Tl-Ba-Ca-Cu-O [1] was quickly followed by the identification [2-8] of two homologous series of phases with the general nominal formulae $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ (single TlO layers) and $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ (double TlO layers) with $1 \leq n \leq 5$. These phases have superconducting $Ca_{n-1}(CuO_2)_n$ layers separated by rocksalt layers.

Similarly, several bismuth compounds with double BiO layers are known and have general nominal composition $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ ($1 \leq n \leq 3$) [9,10]. However no similar materials with a BiO monolayer was known. Recently a Bi cuprate with composition $(Bi_{0.5}Cu_{0.5})Sr_2YCu_2O_7$ has been reported by Ehmann et al [11]. It was claimed that the material had the 1212 structure (Figure 1) and so would be the first reported member of the BiO monolayer series. The 1212 structure was confirmed by several other groups [12,13]. It should be noted, however, that this material is not strictly analogous to the Tl-1212 phase since it contains mixed (Bi/Cu)O layers.

Alternatively the material can be considered as a 123 (or YBCO) type structure with 1/2 Cu1 site substituted by Bi. The 1212 and 123 structures are closely related, with the 4 co-ordinate Cu 'chain' sites in 123 being replaced by approximately octahedrally co-ordinated metal ions, by movement of the oxygen in the basal plane from the face edge towards the face centre. The structure generally assumed for the Bi-1212 material is based on X-ray diffraction data with the basal oxygen confined to the face centre (1c site). Due to the insensitivity of X-ray diffraction to O atoms in the presence of heavy metals such as Bi, we have carried out a structural investigation using time of flight powder neutron diffraction on the material $(Bi_{0.35}Cu_{0.65})Sr_2YCu_2O_7$ with the objective of confirming the general structure and obtaining a more detailed description of the O position in the basal plane.

The material was reported to be non-superconducting as made, but superconductivity has been achieved using certain annealing conditions [11].

Sample Synthesis and Characterisation

High purity Y_2O_3, $SrCO_3$, CuO and Bi_2O_3 were used to make samples of composition $(Bi_xCu_{1-x})Sr_2YCu_2O_7$ for x=0.2-0.5 in 0.05 increments. The samples were heated in air at 985°C for 14hrs and then furnace cooled to room temperature. The purity of the samples was then checked by powder X-ray diffraction (Siemens D5000) with further heat treatments as required, under the same conditions, until a consistent X-ray diffraction profile was obtained. It was found that the optimum Bi content for phase stability was $(Bi_{0.35}Cu_{0.65})Sr_2YCu_2O_7$, which is in good agreement with the results of Beales et al [12]. Iodometric titrations showed the oxygen content to be 7.0

Results and Discussion

Time-of-flight neutron powder diffraction data were collected on $(Bi_{0.35}Cu_{0.65})Sr_2YCu_2O_7$ using the diffractometer POLARIS at ISIS, Rutherford Appleton Laboratory. Data in the range $0.5Å<d<2.25Å$ were used for the structural refinement, using the program TF15LS which is based on the Cambridge Crystallographic Subroutine Library [15,16]. The space group P4/mmm was adopted with initial atomic positions based on the idealised 1212 structure proposed by Ehmann and scattering lengths of Y=0.7750, Bi=0.8533, Sr=0.7020, Cu=0.7718 and O=0.5805 (all x10^{-12}cm).

Early refinements gave high temperature factors for Bi/Cu1, O1 and O4 (see Figure 1). The high temperature factor for the O1 site was consistent with the possible displacement of the O from the face centre site towards the face edge. The O1 was therefore allowed to move off this site in the [010] direction. This reduced the temperature factor and R-factors. However, since the temperature factor was still higher than expected, anisotropic temperature factors were introduced for this site. Refinement resulted in a high value for B_{22} (2.417Å^2) showing that most disorder is directed along the b-axis. This is not unexpected due to the different co-ordination preferences of the Bi and Cu cations in the adjacent Bi/Cu1 site. It has been reported by Slater and Greaves [14] that in some similar 1212 type phases the O1 site was, in fact, split into two (O1 and O1'). The structure was therefore refined with two separate O1 sites, but refinements indicated preferential occupancy of a single site, and subsequent examination assumed one O1 position with anisotropic thermal parameters. The introduction of anisotropic temperature factors for O4 resulted in a high B_{33} value which again is consistent with mixed cation occupancy of the Bi/Cu1 site. The Bi/Cu1 site was also allowed to move in the [010] direction, as had been observed in other phases, and this produced an acceptable isotropic temperature factor . Results of the final refinement are given in Table 1 and selected bond distances in Table 2.

Basic Bond Valence Sum calculations were carried out on the refined structure to obtain some insight into the oxidation states of the Cu1 and Bi. Refinements can clearly only reflect the average structure and so the results of the calculations must be viewed with some caution. Considering first the Bi-O polyhedra, since the two Bi-O4 distances are very short and alone suggest a Bi oxidation state of 3.6+, it was therefore assumed that Bi was present as Bi^{5+}. This is in agreement with Beales who proposed that chemically stable 1212 phases were generally observed when the average valency in the rocksalt layer is +3 and so a 2:1 ratio of Cu:Bi would imply Cu^{2+} and Bi^{5+}.

For simplicity the Bi/Cu1 site was constrained to its original (0,0,0) position as the displacement of the site appeared to have only a minor effect on the calculations, compared to that of the O1 displacement. Considering only the displacement of the O1, the Bi can have either a short or longer bond to O1 depending on whether the O1 is displaced towards (O1a) or away (O1b) from the Bi (Figure 2). Our calculations have demonstrated that a Bi co-ordination of 6 (with 4 short (O1a) bonds) would be consistent with an oxidation state of 5+ (Bond Valence Sum=+4.99).

In the absence of a knowledge of the detailed microstructure, even with 4 Bi-O1a bonds, the Cu stereochemistry cannot be reliably deduced. However, it is clearly impossible for the Cu to have 3 or 4 short Cu-O1 bonds. The remaining possible situations give bond valence sums of 1.4 (1 short and 3 long bonds) and 1.63 (2 short and 2 long bonds). This suggests the possibility that some of the Cu1 might be present as Cu^{1+} linearly co-ordinated to two O4 with 4 longer (3.59Å) O1b bonds not really affecting the co-ordination. Interestingly BVS calculations for the Cu2 site produce a value of +2.27 which might be consistent with this view but it must be realised that it could equally indicate simple 'overbonding' at this site [17]. Moreover, the redox properties of Bi^{5+} and Cu^{+} suggest that their coexistence within the same layer is improbable. A more likely explanation for this is that the Bi/Cu1-O4 bond actually consists of a shorter Cu-O4 bond and a longer Bi-O4 bond, with the refinement only showing the average position of the two possible O4 sites. This would be consistent with the high O4 anisotropic temperature factor, B_{33}, and would result in the true Cu oxidation state being higher than the value calculated.

More recent work focused on the related material $(Ce/Cu)Sr_2YCu_2O_7$. Using the guidelines proposed by Beales it was expected that the phase $(Ce_{0.5}Cu_{0.5})Sr_2YCu_2O_7$ would be the most stable phase. This was found to be correct although the material was still not single phase. The material was found to be non superconducting as expected and Ca doping on the Y site resulted in increased impurity phases with no change in the superconducting properties. Small amounts of Ba doping on the Sr sites dramatically improved the phase purity, with the ideal composition found to be $(Ce_{0.5}Cu_{0.5})Sr_{1.8}Ba_{0.2}YCu_2O_7$. The introduction of Ba also induced superconductivity in the material with the highest T_c observed at 62K although conditions have not yet been optimized. Further work is focusing on improving phase purity and T_c in these materials and we hope to carry out a neutron diffraction study in the near future.

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Table 1
Refined structural parameters for $Bi_{0.35}Cu_{0.65}Sr_2YCu_2O_7$
Estimated standard deviations are given in parentheses

ATOM	POS	X	Y	Z	B(Å^2)	UNIT CELL OCCUPANCY
Y	1d	0.5	0.5	0.5	0.50(2)	1.0
Sr	2h	0.5	0.5	0.2024(1)	1.00(2)	1.0
Cu2	2g	0.0	0.0	0.3582(1)	0.31(1)	1.0
Bi	4l	0.0	0.0730(7)	0.0	0.81(5)	0.0875
Cu1	4l	0.0	0.0730(7)	0.0	0.81(5)	0.1625
O1	4n	0.5	0.296(2)	0.0	*	0.25
O3	4i	0.5	0.0	0.3764(1)	0.64(2)	1.0
O4	2g	0.0	0.0	0.1603(2)	*	1.0

a=b=3.814(1)Å, c=11.714(3)Å; P4/mmm
R_I=6.0%, R_p=3.54%, R_{wp}=3.47%, R_{exp}=1.45%

* Anisotropic temperature factors (Å^2)

Atom	B_{11}	B_{22}	B_{33}
O1	1.8(2)	2.4(2)	1.3(2)
O4	1.40(4)	1.40(4)	1.87(8)

Table 2
Selected Bond Distances (Å)

Bi/Cu1-O1a	2.216(8)
Bi/Cu1-O1b	3.585(8)
Bi/Cu1-O4	1.877(4) [x2]
Cu2-O3	1.919(2) [x4]
Cu2-O4	2.318(3)

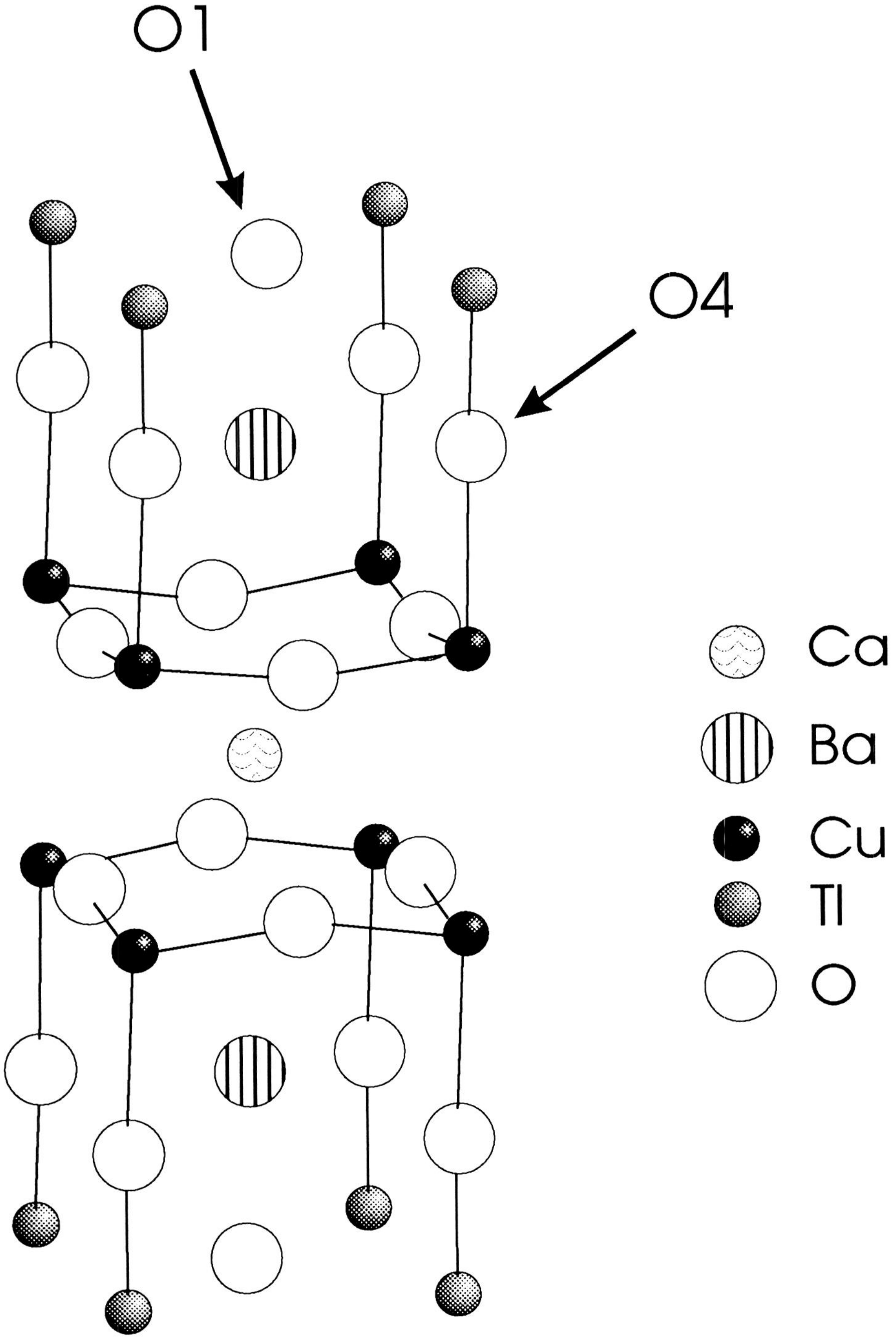

Figure 1.- The basic 1212 structure for $T1Ba_2CaCu_2O_7$.

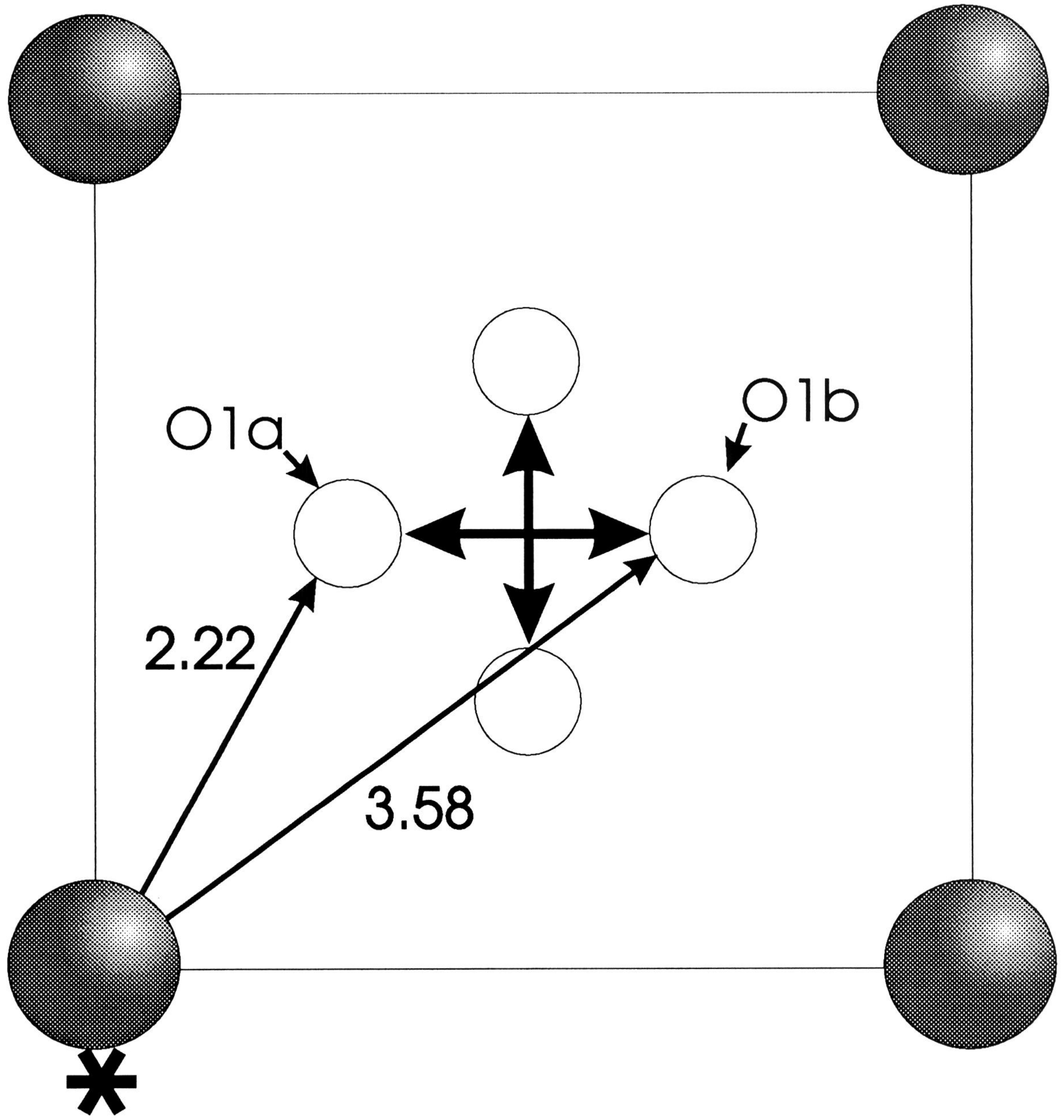

Figure 2.- The basal plane of the refined structure showing the possible positions of the O1 site with respect to the cation marked*. All bond lengths in Angstroms