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A Neutron Diffraction Study of $LaBa_2Cu_3O_{7-\delta}$

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The correlation between structure and oxygen content in the $LaBa_2Cu_3O_{7+\delta}$ was investigated by neutron powder diffraction. It is shown that the structure is orthorhombic (*Pmmm*) when $\delta = -0.04$ and tetragonal (*P4/mmm*) when $\delta = -0.06$. Such a change in structure accompanying a very small variation in oxygen stoichiometry is remarkable. In the orthorhombic structure of the $\delta = -0.04$ sample, there is 70% oxygen occupancy for the linear chain site (0, $\frac{1}{2}$, 0) and 34% for the ($\frac{1}{2}$, 0, 0) site. The La sites have 13.6% Ba when $\delta = -0.04$ and 11.2% Ba when $\delta = -0.06$; the Ba sites have 10% La in both cases.

The influence of oxygen stoichiometry on the superconductivity of $YBa_2Cu_3O_{7-\delta}$ has been investigated in great detail (*1–4*). The structure of $YBa_2Cu_3O_{7-\delta}$ remains orthorhombic up to a δ of ~0.06, at which composition the structure becomes tetragonal. The T_c of $YBa_2Cu_3O_{7-\delta}$ shows a marked dependence on oxygen stoichiometry. In the δ range 0.0–0.2, the T_c remains around 90 K; in the δ range 0.2–0.4, the T_c shows a plateau at 55 ± 5 K although the structure continues to remain orthorhombic (Fig. 1a). Recently, a sample of $YBa_2Cu_3O_{7.1}$ with some oxygen excess was prepared by a low-temperature method. This sample, although tetragonal, showed a T_c of ~55 K (*5*). It may, therefore, be surmised that the T_c of $YBa_2Cu_3O_{7-\delta}$ remains relatively high (50–90 K) over the entire range of δ between −0.01 and +0.4 (Fig. 1a). In the orthorhombic structure of $YBa_2Cu_3O_{7-\delta}$ and related 123 oxides, the oxygen sites along the *b*-axis (01 sites) are predominantly populated; nearly equal population of 01 and 05 sites (along the *b*- and *a*-axes) results in a tetragonal structure (*1, 6, 7*).

We recently investigated the $LaBa_2Cu_3O_{7-\delta}$ system in some detail (*7*) and found that the orthorhombic structure as well as high-temperature superconductivity occur over a very narrow range of oxygen stoichiometry. In this oxygen-excess samples (negative δ) are more readily obtained than in $YBa_2Cu_3O_{7-\delta}$. Careful measurements of T_c at a function of δ (determined by thermogravimetry) in $LaBa_2Cu_3O_{7-\delta}$ have shown the behavior illustrated in Fig. 1b. We see that, unlike in the $YBa_2Cu_3O_{7-\delta}$

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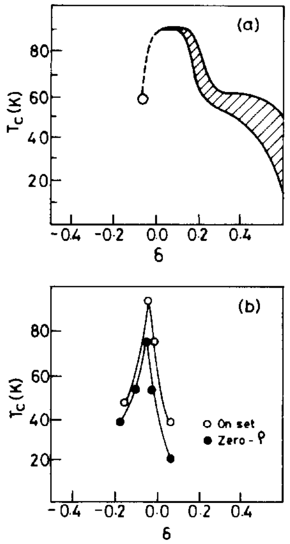

FIG. 1. Variation of T_c with δ in (a) $YBa_2Cu_3O_{7-\delta}$.

system, T_c varies sharply with δ in $LaBa_2Cu_3O_{7-\delta}$. T_c drops drastically even with a variation of 0.05 in δ. Furthermore, orthorhombicity manifests itself only in the composition range where high T_c is found. Although the δ values determined by thermogravimetry are subjected to some uncertainty (± 0.05), the general variation of T_c with δ is very significant. In order to find whether there is a structural change in $LaBa_2Cu_3O_{7-\delta}$ with a small change in δ, we investigated the structures of two closely lying compositions of $LaBa_2Cu_3O_{7-\delta}$ by neutron diffraction profile analysis. It may be noted here that it is only by neutron diffraction studies that we can unequivocally establish the structures of such oxides where the location of the oxygens crucially determines the structure. The present study has indeed established that the structure of $LaBa_2Cu_3O_{7-\delta}$ changes from orthorhombic to tetragonal with a minor change in δ accompanied by changes in the occupation of the 01 and 05 sites.

The La–Ba–Cu–O compositions were prepared by heating appropriate mixtures of La_2O_3 (preheated at 1200 K and cooled in a desicator), $BaCO_3$, and CuO at 1225 K for 24 hr. The resulting product was annealed at 1200 K for 24 hr and slowly cooled in air (sample I). Sample II was prepared by the same method except that it was further heated in oxygen at 775 K for 24 hr. X-ray diffraction pattern of both samples recorded with Cu*Kα* radiation with silicon as external standard showed them both to be tetragonal with $a = 3.93$ Å and $c = 11.78$ Å. These two samples were subjected to neutron diffraction studies. Neutron diffraction patterns were recorded at room temperature at a wavelength, $\lambda = 1.2105(1)$ Å, using the newly installed diffractometer (*8*) (T-1011) at the 100 MW DHRUVA reactor at Trombay. Sample I ($LaBa_2Cu_3O_{7.04}$) was in the form of powder (18.2 g) in a Ti–Zr container (16 mm diameter) while sample II ($LaBa_2Cu_3O_{7.06}$) was in the form of a cylindrical pellet (15.2 g, 15 mm diameter, 18 mm high). The instrument collimations were 0.7°–0.5°–0.7° from the in-pile to the detector end. The observed patterns from the two samples are given in Figs. 1 and 2, respectively.

The neutron patterns were analyzed by the Rietveld profile analysis method, using a modified version of the program DBW 3.2 (*9*). To start with, the tetragonal space group *P4/mmm* was assumed to refine the structures of both samples. All possible positional, thermal (*B*), and occupancy (*N*) parameters were varied. A Gaussian peak shape function was assumed. The scattering lengths used were 8.3, 5.2, 7.6, and 5.75 fermi for La, Ba, Cu, and O, respectively. Due to limited nature of the data, there were strong correlations between the thermal and the occupancy parameters of individual atoms, and consequently they had to be refined alternately. In the final stages of the refinement, some of the thermal and occupancy parameters (labeled with F within parentheses in Table I) were kept fixed at their optimum values. Other variables included in the refinement were cell parame-

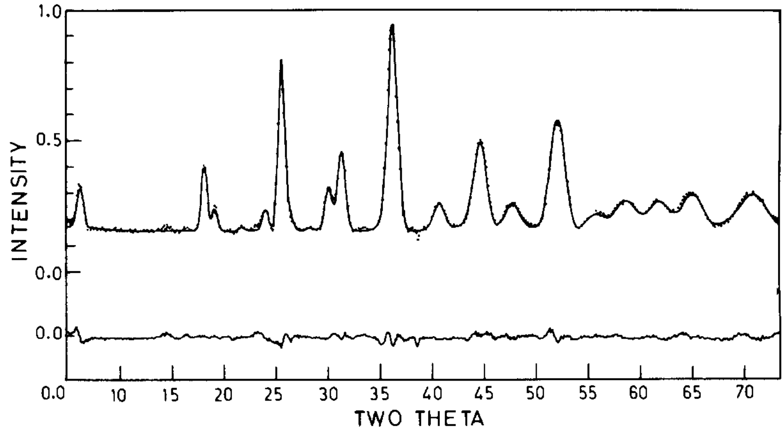

FIG. 2. Profile fit and difference plot for $LaBa_2Cu_3O_{7.04}$.

ters, three half-width parameters, zero-point, scale factor, and six background parameters. The structures of both samples refined well with the tetragonal space group *P4/mmm*. The resulting structural parameters and the residuals are listed in Table I.

Further structure refinements were attempted using the orthorhombic space group *Pmmm* and starting with the final parameters obtained from the *P4/mmm* refinements. This involved an increase of three variable parameters, because the *B* values for O(1) and O(5) were constrained to be equal, as for O(3) and O(4) also. The use of the orthorhombic space group *Pmmm* led to significant improvement in the *R* values for sample I, but no improvement could be obtained for sample II. The structural parameters for sample I obtained with *Pmmm* are also given in Table I. Significance tests on the *R* factor ratio indicated that the space group *P4/mmm* could be rejected in favor of *Pmmm* at a significance level of better than 0.5% for sample I.

We, therefore, conclude that $LaBa_2$

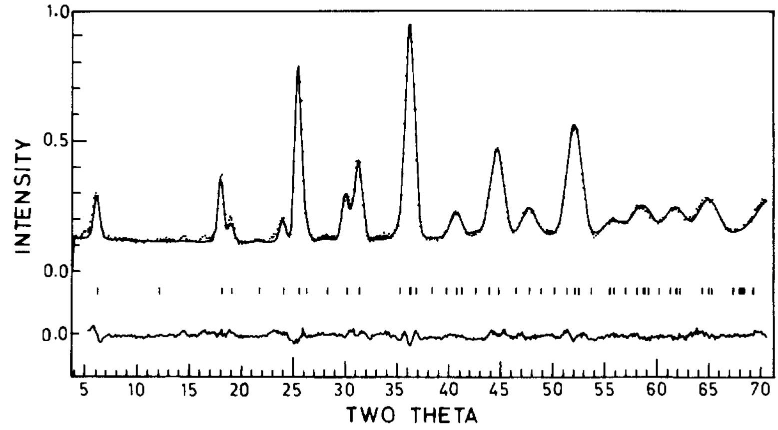

FIG. 3. Profile fit and difference plot for $LaBa_2Cu_3O_{7.06}$.

TABLE I

ATOMIC POSITIONAL, THERMAL, AND OCCUPANCY PARAMETERS IN THE TWO $LaBa_2Cu_3O_{7-\delta}$ SAMPLES

Parameter		Sample I		Sample II
Space	group	*P4/mmm*	*Pmmm*	*P4/mmm*
	a	3.916(1)	3.900(2)	3.917(1)
	b	= *a*	3.931(2)	= *a*
	c	11.797(6)	11.787(6)	11.768(6)
	R_p (%)	2.95	2.89	3.38
	R_{wp} (%)	3.83	3.76	4.42
	R_B (%)	1.12	1.10	1.23
Cu(1)	*x*	0	0	0
	y	0	0	0
	z	0	0	0
	B	0.60(24)	0.67(19)	0.79(24)
	N	0.125(F)	0.125(F)	0.125(F)
Cu(2)	*x*	0	0	0
	y	0	0	0
	z	0.3458(6)	0.3460(7)	0.3476(6)
	B	0.49(F)	0.49(F)	0.49(F)
	N	0.25(F)	0.25(F)	0.25(F)
Ba/La	*x*	0.5	0.5	0.5
	y	0.5	0.5	0.5
	z	0.1800(7)	0.1797(7)	0.1808(7)
	B	0.65(F)	0.65(F)	0.65(F)
	N	0.265(3)	0.224/0.026(5)	0.224/0.0265(5)
La/Ba	*x*	0.5	0.5	0.5
	y	0.5	0.5	0.5
	z	0.5	0.5	0.5
	B	0.56(F)	0.56(F)	0.56(F)
	N	0.119(2)	0.108/0.017(4)	0.111/0.014(4)
O(1)	*x*	0	0	0
	y	0.5	0.5	0.5
	z	0	0	0
	B	2.38(F)	2.38(F)	3.0(F)
	N	0.130(3)	0.088(8)	0.132(3)
O(2)	*x*	0	0	0
	y	0	0	0
	z	0.1585(9)	0.1588(9)	0.1590(9)
	B	0.88(27)	0.85(27)	1.32(29)
	N	0.25(F)	0.25(F)	0.25(F)
O(3)	*x*	0.5	0.5	0.5
	y	0	0	0
	z	0.3671(4)	0.3688(25)	0.3667(5)
	B	0.65(18)	0.62(13)	0.69(17)
	N	0.50(F)	0.25(F)	0.50(F)
O(4)	*x*	—	0	—
	y	—	0.5	—
	z	—	0.3653(27)	—
	B	—	0.62(13)	—
	N	—	0.25(F)	—
O(5)	*x*	—	0.5	—
	y	—	0	—
	z	—	0	—
	B	—	2.38(F)	—
	N	—	0.042(8)	—

Note. The estimated standard deviations are given in parentheses; F implies the parameter was kept fixed at the optimum value. Number of atoms per formula unit is equal to 8N.

TABLE II

INTERATOMIC DISTANCES (Å) IN THE TWO $LaBa_2Cu_3O_{7-\delta}$ SAMPLES

	Sample I ($\delta = -0.04$) *Pmmm*	Sample II ($\delta = -0.06$) *P4/mmm*
Ba/La–O(1)	2.879(6) . . (×1.408)	2.892(6) . . (×2.112)
–O(2)	2.780(2) . . (×4)	2.782(1) . . (×4)
–O(3)	2.972(23) . . (×2)	2.936(8) . . (×4)
–O(4)	2.931(24) . . (×2)	—
–O(5)	2.890(6) . . (×0.672)	—
La/Ba–O(3)	2.501(18) . . (×4)	2.509(4) . . (×8)
–O(4)	2.515(20) . . (×4)	—
Cu(1)–O(1)	1.966(1) . . (×1.408)	1.959(1) . . (×2.112)
–O(2)	1.872(11) . . (×2)	1.871(11) . . (×2)
–O(5)	1.950(1) . . (×0.672)	—
Cu(2)–O(2)	2.207(13) . . (×1)	2.219(13) . . (×1)
–O(3)	1.968(4) . . (×2)	1.971(1) . . (×4)
–O(4)	1.979(4) . . (×2)	—

$Cu_3O_{7.04}$ (sample I) has the disordered orthorhombic structure, while $LaBa_2Cu_3O_{7.06}$ (sample II; see Fig. 3) has the disordered tetragonal structure, thereby indicating that the structural transformation from the orthorhombic to the tetragonal symmetry in La–Ba–Cu–O system occurs when the oxygen content is between 7.04 and 7.06. Interestingly, T_c is also highest around this composition. The refined values of the occupancy parameters indicate that 10% of the Ba sites are occupied by La in both samples, while 13.6% of La sites in sample I and 11.2% in sample II are occupied by Ba. The somewhat higher La content of sample II is consistent with its higher oxygen content (7.06) relative to sample I. The interatomic distances in the two compounds listed in Table II however do not indicate any notable differences.

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