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Effect of structural changes on the zero-resistance transition temperature of $La_1Ba_2Cu_3O_{9-\delta}$

Sung-Ik Lee, John P. Golben, Sang Young Lee, Xiao-Dong Chen, Yi Song, Tae W. Noh, R. D. McMichael, J. R. Gaines, D. L. Cox, and Bruce R. Patton
Department of Physics, Ohio State University, Columbus, Ohio 43210

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A series of high-T_c $La_1Ba_2Cu_3O_{9-\delta}$ superconductors with zero resistance in the range from 27 to 69 K has been synthesized. The variance in T_c is related to structural changes as observed through x-ray diffraction analysis. Of particular importance is the increase in the intensity of the (014)/(005) superlattice peak with an increase in T_c, and evidence of orthorhombic shouldering for the highest-T_c samples. The change in the intensity of the (014)/(005) line can be explained by the movement of atomic positions brought about by oxygen deficiencies.

The first reports of high T_c (zero resistance) transition temperatures in the La-Ba(Sr)-Cu-O system initiated a wave of interest in this field.[1,2] The superconducting phase of these materials was found to be a K_2NiF_4 layered perovskite,[3,4] with complete zero resistance achieved at temperatures of 12 and 35 K for the Ba-doped and Sr-doped samples,[1,2,4] respectively. A few theoretical papers have already been written to try to explain the inherent superconducting mechanism[5-7] in these compounds. More recently, superconductivity was discovered in the Y-Ba-Cu-O system, with a $Y_1Ba_2Cu_3O_{9-\delta}$ single-phase perovskite structure and complete zero resistance in the range of 90 K.[8,9] This discovery has raised new theoretical questions and has encouraged a search for other high-T_c superconductors, including a return to the La-Ba constituents. In this paper we focus on the new high-T_c superconductor $La_1Ba_2Cu_3O_{9-\delta}$. With slight changes in the sample preparation conditions, we have obtained samples with zero resistance in the range from 27 to 69 K, and with T_{c0}'s extending to 83 K. For a group of samples primarily synthesized by the coprecipitation method, we found the x-ray spectra to be free from other major phases such as $BaCuO_2$. These "impurity"-free samples exhibited an increase in the intensity of the (014)/(005) line with the increase in T_c, allowing for a systematic correlation between the structural changes and the transition temperature. Evidence of orthorhombic shouldering in samples with T_c's from 63 to 69 K indicates that a sequential orthorhombic phase may be necessary for 90-K superconductivity.

Though they possess different stoichiometries, the high-T_c compounds $La_{1.85}Ba_{0.15}CuO_4$ and $Y_1Ba_2Cu_3O_{9-\delta}$ are similar in the respect that they both have oxygen-deficient perovskite structures containing CuO_2 planes.[3,10-16] These planes, and more specifically the Cu-O interaction, have been singled out as inherently important to the superconducting mechanism in these compounds.[10-16] Changes in this interaction can be brought about by various oxygen locations and amounts, since the oxygen deficiencies will change the valence structure as well as dictate changes in the bond lengths between the cell constituents. For the Cu-O interaction, a relation between T_c and the Cu-O bond length has been reported for the K_2NiF_4 compounds.[17] Simultaneous studies on the La_2CuO_4 compound show that while this compound is an insulator at low temperatures, doping with Ba or Sr suppresses the metal-insulator transition and changes the room-temperature cell structure from orthorhombic to tetragonal. The structural change is accompanied by a reduction in the Cu-O bond distance.[18] The actual superconducting mechanism may not be inherently involved with the structural changes alone, i.e., the structural changes may only be a by-product of some deeper correlation such as the valence changes due to the oxygen deficiencies. However, relating T_c to structural changes may help to pinpoint the actual superconducting mechanism.

The proposed unit cell for the well-studied single-phase superconductor $Y_1Ba_2Cu_3O_{9-\delta}$ is an orthorhombic, oxygen-deficient perovskite structure with space group *Pmmm*.[14,16] The Ba and Y atoms are ordered in a Ba-Y-Ba sequence along the c axis forming a triplet cell with c almost equal to $3a$.[10-16] This structure has been identified by electron diffraction,[19] x-ray diffraction,[11-15] and neutron scattering.[16] We will call this order structure the "sequential orthorhombic" structure. From the analysis of the x-ray d spacings, we have identified this structure to be present in all of our "90-K" superconductors, namely, those based on Y-Ba, Er-Ba,[20] Ho-Ba,[21] and Gd-Ba. The insensitivity of 90-K superconductivity to the magnetic rare-earth elements in the latter three compounds suggest that the superconducting electrons are spatially separate from the rare-earth ions.[22] All of the present evidence indicates that a sequential ordered phase is required for 90-K superconductivity, while the importance of the specific rare-earth metal that is substituted is minimal.

The x-ray diffraction data of our 90-K superconductors are mutually consistent. All of the spectra show orthorhombic splitting and the appearance of distinct superlattice lines between the major peaks. The (014)/(005) superlattice peak is particularly notable since the observed intensity is anomalously large compared to the calculated value, when the calculation assumes an oxygen occupancy of 100% in the unit cell. Full oxygen occupancy further assumes that the Ba atoms sit at the centers of the perovskite subunits ($c/6$ and $5c/6$), while the Cu atoms sit at 0, $c/3$, and $2c/3$. Reitveld refined neutron-diffraction data on the $Y_1Ba_2Cu_3O_{9-\delta}$ compound[16] specified a Ba position change to 0.184*c* and a Cu position change to 0.356*c*, as well as an oxygen deficiency such that the δ as used here is 2.19. When the calculation takes into account these new values, the calculated (014)/(005) line intensity increases by two orders of magnitude. The new calculated value is comparable to the observed value. Better intensity fittings between the observed and calculated values also occur for the other spectral lines, where the original discrepancy was not so large. We shall return to the (014)/(005) superlattice line when we consider the structural changes of $La_1Ba_2Cu_3O_{9-\delta}$.

Our $La_1Ba_2Cu_3O_{9-\delta}$ samples were synthesized by two methods, the solid-state reaction method[9] and the coprecipitation method.[20,21,23] In general, the solid-state reaction method produced samples with the highest T_c's, defined here as the zero-resistance transition temperature, and the highest onset T_{c0}'s, defined here as the knee in the *R* vs *T* plots (Fig. 1). The method of coprecipitation produced samples that were relatively free of the competing major phases such as $BaCuO_2$ that seemed to plague the samples prepared by the solid-state reaction method. Our highest-T_c samples were further prepared in a high-pressure oxygen environment of up to 11 atm, with a characteristic broadening of the transition region such that T_{c0} was considerably higher. However, these samples were unstable with time.

Despite the use of several sample-preparation methods and the manipulation of the preparation conditions, we could only obtain a value of T_c (zero resistance) of up to 69 K for $La_1Ba_2Cu_3O_{9-\delta}$. Other groups have not fared much better, with the highest value reported to date being 75 K, reported by Hor *et al.*[22] Since the onset temperatures for these transitions have been much higher, there is still optimism that a 90-K La-Ba sample will be synthesized. However, when we consider further the comparison of the x-ray spectra with the other "1-2-3" superconductors, there is a unique difference associated with the La-Ba superconductor. As shown in Fig. 2, a typical La-Ba spectrum lacks the orthorhombic splitting of the major peaks that is evident in the spectrum for $Y_1Ba_2Cu_3O_{9-\delta}$; for example, the (206)/(220)/(026) peak. This indicates that the $La_1Ba_2Cu_3O_{9-\delta}$ compound has either a cubic or tetragonal structure. Furthermore, apart from the (014)/(005) superlattice line, the superlattice lines in the La-Ba spectrum have all but disappeared.

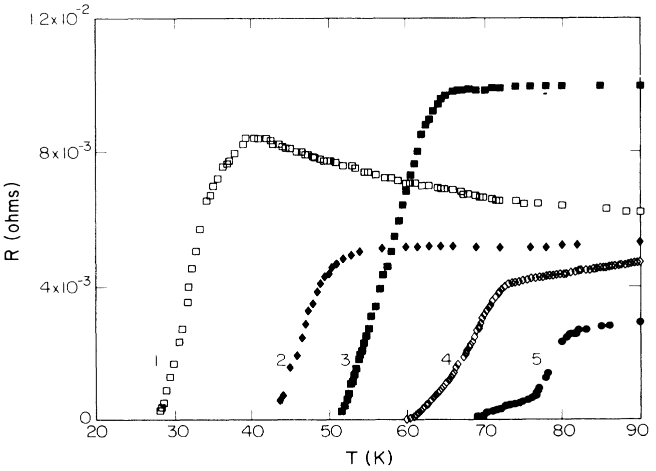

FIG. 1. Electrical resistance vs temperature for five $La_1Ba_2Cu_3O_{9-\delta}$ samples. Samples 1 and 2 were prepared by the coprecipitation method and samples 3–5 were prepared by the solid-state reaction method. Except for sample 1, which was sintered at 925 °C, all samples on this graph were sintered at 950 °C for 12 h or more. Samples 1, 3, and 4 were annealed at 500 °C in the presence of O_2 while samples 2 and 5 were further prepared in a high-pressure O_2 atmosphere (11 atm).

Since the La and Ba atoms have similar x-ray cross sections, one possibility for the observed spectrum would be that the structure has a sequential tetragonal unit cell. Particular evidence for the existence of the sequential tetragonal structure in this compound is the finite intensity of the lone superlattice line (014)/(005). In fact we found that the intensity of this line correlates to the change in T_c, as long as the spectrum is not infiltrated by impurity phase lines. When presented as a percentage of the major peak in the spectrum, the intensity of this (014)/(005) line is 3.3% when T_c is 27 K, 4.2% when T_c is 37 K, 4.4% when T_c is 48 K, and 4.8% when T_c is 56 K.

We consider two possible explanations for the observed correlation between the (014)/(005) peak intensity and T_c. The first possibility is that the intensity changes as a result of atomic displacements within the unit cell and that T_c is also dependent upon these structural movements. Specifically, assuming a sequential tetragonal structure, a positional change of the Ba atoms will primarily affect the intensity of the (014)/(005) line. The movement of these atoms is in turn inherently related to the amount and location of the oxygen deficiencies in the unit cell. It is noted that the O atoms have small x-ray scattering power, and the positions of the La atoms are fixed by symmetry. Thus the Ba positions serve as the yardstick for the structural changes (though some displacement of the Cu atoms near $c/3$ may be necessary as

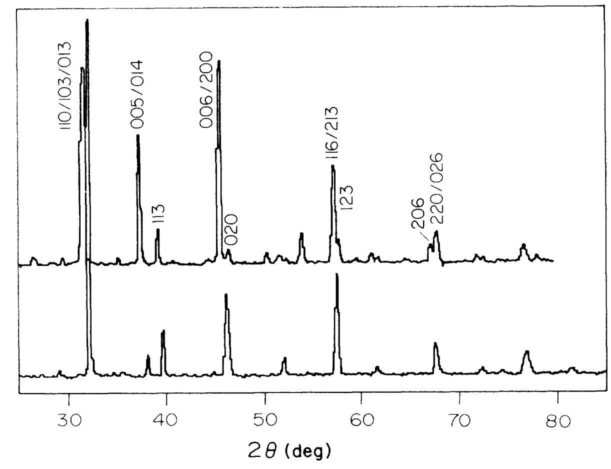

FIG. 2. The x-ray spectra of $Y_1Ba_2Cu_3O_{9-\delta}$ (above) and $La_1Ba_2Cu_3O_{9-\delta}$ (below) is presented. Note the appearance of superlattice lines between the main spectra for the Y series. The splitting of some of the major peaks for the $Y_1Ba_2Cu_3O_{9-\delta}$ is discernable even from this low resolution plot. This splitting is not resolvable in the spectra for $La_1Ba_2Cu_3O_{9-\delta}$.

well). If we infer that T_c is directly dependent upon the oxygen deficiency, then the change in the intensity of the (014)/(005) line is a natural consequence of this dependence.

The second possibility that we have considered is that the La-Ba samples consist of a sequential tetragonal phase that competes with an "impurity" cubic phase. For the structure to appear cubic, it is necessary for the La and Ba atoms to randomly distribute themselves at the centers of the unit cells. We refer to this proposed structure as the "random cubic phase."[24] The calculated lattice constants for both possible structures are close; $a = 3.9166$ and 3.9134 Å for the cubic and tetragonal structures, respectively. The change in T_c with the intensity of the (014)/(005) line could be the result of a mixture of these two phases.

While such an "impurity" random phase has been suggested to occur for $Y_1Ba_2Cu_3O_{9-\delta}$ samples as well,[25] we believe that this explanation is less feasible than the first explanation relating T_c to the atomic displacements in the unit cell. Since the proposed random phase would most probably involve a random distribution of oxygen deficiencies as well, causing small random lattice distortions, we would expect to see a significant broadening of the major peaks in the x-ray spectrum. Instead, our diffraction data show no essential broadening over a reference 90-K superconductor. This broadening would not be observed if we assumed that there was full oxygen occupancy (O_9), but this situation is very unlikely since all of our samples were consistently free of anomalous broadening, despite different oxygen preparation conditions. Full oxygen occupancy would also require an unphysically high nominal Cu valence.

We should note here that we also synthesized many samples that contained significant amounts of well-known impurity phases. In particular, the major peaks for $BaCuO_2$ were usually found near $2\theta = 30°$. Though the value of T_c still tended to correlate with the (014)/(005) line intensity, the correlation in this case was not totally consistent. We also have observed T_c to decrease in samples of $Er_1Ba_2Cu_3O_{9-\delta}$ and $Ho_1Ba_2Cu_3O_{9-\delta}$ when competing phases became more prevalent in those samples.[20,21] A comparison of the published spectra of $Y_1Ba_2Cu_3O_{9-\delta}$ (Refs. 26 and 27) along with the spectra of our own coprecipitated Y-Ba samples, also shows a tendency for the (014)/(005) line intensity and T_c to reduce as the competing phases become more prevalent. However, a totally consistent picture is not expected since the emergence of competing phases severely complicates the analysis.

Finally it is noted that T_c depends on preparation effects which are as yet not understood. One observation is that our solid-state-reacted samples had higher T_c's than our coprecipitated samples. This was true in general for the La-Ba series, despite the fact that the solid-state reacted samples most often had competing phases such as $BaCuO_2$. Another observation is that our highest T_c samples in the range of 63 to 69 K, albeit with impurity phases present, all showed evidence of orthorhombic shouldering on the major peaks. It is therefore possible that a change from the tetragonal structure to an orthorhombic structure is needed in order to obtain a "90-K" T_c. If this explanation is correct, then the universal tendency for the sequential orthorhombic "1-2-3" compounds to have 90-K T_c's would be kept intact.

In summary, we have synthesized a sequence of tetragonal $La_1Ba_2Cu_3O_{9-\delta}$ samples by different preparation techniques, for which the zero resistance T_c varies from 27 to 69 K. In samples without competing phases, the intensity of the (014)/(005) tetragonal x-ray diffraction peak increases with the transition temperature. The observed intensity changes can be explained by atomic displacements in the unit cell due to oxygen deficiencies.

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