Thermogravimetric study of the La₁Ba₂Cu₃O_{7- δ} system: The correlation of T_c with oxygen content

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We report a systematic study of a series of single-phased La₁Ba₂Cu₃O_{7- δ} samples where the oxygen content was determined by thermogravimetric analysis. The highest zero-resistance T_c was 72 K, corresponding to $\delta = 0.25$. An increase in δ reduced T_c to 44 K, similar to the behavior reported for Y₁Ba₂Cu₃O_{7- δ}. This is consistent with the idea that, as oxygen is taken away from the planes where Cu-O chains exist, T_c is reduced. For samples where the oxygen content was increased *until* δ became negative, T_c decreased to a value as low as 23 K, presumably due to increased La-Ba disorder. These samples with low T_c and high oxygen content have apparent tetragonal x-ray spectra, suggesting that Cu-O chain ordering has been further disrupted and that the oxygen occupancy on these planes has increased.

Extensive experimental studies have been focused on the high- T_c superconductor $Y_1Ba_2Cu_3O_{7-\delta}$. Detailed neutron studies on this^{1,2} compound as well as several structural studies on 1:2:3 compounds with Y replaced by rare-earth elements, 3,4 have associated the orthorhombic sequential structure with high zero-resistance T_c 's near 90 K. The orthorhombicity is attributed to the ordering of oxygen vacancies in the copper planes between the Ba layers such that ordered Cu-O chains remain. While the exact role of these Cu-O chains is unclear, they are thought to be important to the high superconducting transition temperature either directly or through their interaction with the inner Cu-O sheets. Recently, considerable attention has been focused on the compound $La_1Ba_2Cu_3O_{7-\delta}$ and its variations where different levels of lanthanum are doped into the barium sites.⁵⁻¹⁷ X-ray spectra on samples of the La₁Ba₂Cu₃O_{7- δ} compound with low T_c's have been reported to appear tetragonal, although orthorhombic shouldering has been observed in samples with T_c 's above 60 K.⁵ Further x-ray studies on samples of La₁Ba₂Cu₃O_{7- δ} with zero resistances as high as 80 K concluded that the samples with high T_c 's were indeed orthorhombic.^{6,7} This strengthens the idea that ordered Cu-O chains play a very important role in these so-called 1:2:3 superconducting $R_1Ba_2Cu_3O_{7-\delta}$ (R is Y, La, and other rare-earth elements) materials, and that for these samples with T_c 's approaching the 90-K plateau, an orthorhombic structure is required.

The importance of the Cu-O chains has been questioned by the observation that there exist certain La₁Ba₂Cu₃- $O_{7-\delta}$ samples that possess an apparent tetragonal structure but still become superconductors below 40 K. While several quenching studies on the Y₁Ba₂Cu₃O_{7- $\delta}$ compound have suggested an empirical relation between the orthorhombic distortion and T_c (with the tetragonal phase being nonsuperconducting), a similar relationship has yet to be established in La₁Ba₂Cu₃O_{7- δ}. In this paper, we report a systematic study of the dependence of T_c on the oxygen content (x) in La₁Ba₂Cu₃O_{7- δ} samples as measured} by thermogravimetric analysis (TGA). The samples are predominantly single-phased with T_c 's ranging from 23 to 72 K. Our highest zero-resistance transition temperature of 72 K corresponds to an oxygen content of $x=7-\delta$ =6.75. From that point, as the oxygen content decreases so does T_c until it reaches the value 44 K, consistent with the trend found in $Y_1Ba_2Cu_3O_{7-\delta}$.¹⁸ What is quite surprising (and different from the yttrium system), is that for oxygen content x greater than 7, the value of T_c also decreases. Combined with what is known about the structure of this compound and that of $Y_1Ba_2Cu_3O_{7-\delta}$, the present results suggest that (i) Cu-O ordering is important for T_c 's in the range 44-72 K with the reduction in T_c scaling with the reduction in oxygen content (and increased oxygen disorder) as it does in the Y-Ba-Cu-O system and (ii) for an oxygen content greater than 7, increased oxygen occupancy on the outer Cu-O planes introduces an additional disorder that further reduces T_c from the peak value of 72 to 23 K.

The samples used in this study were prepared by the solid-state-reaction method. The initial La₂O₃, BaCO₃, and CuO powders were mixed according to the appropriate stoichiometry. After baking and grinding twice, the powders were pressed into pellet form. The final sintering was performed in flowing oxygen with the sintering temperature ranging from 950 to 1000 °C. The samples were slowly cooled to 500 °C and further annealed in oxygen at that temperature for at least 12 h. The general sample preparation procedures have been outlined in detail elsewhere.¹⁹

The samples were characterized by use of powder x-ray diffraction. All samples were predominantly single phased with small traces of $BaCuO_2$ in some samples (<5%). Resistance measurements were made using the four-probe ac method. Thermogravimetric analysis (TGA) measurements were performed on a Perkin-Elmer 7 series thermal analysis system. The reducing atmosphere used was a mix of 5% hydrogen and 95% nitrogen. The gas flow rate was 0.02 ft³/h and the heating rate was

20 °C/min. Visually, the final product was a porous pumice with the color and consistency of metallic copper.

A typical measurement of a sample with $T_c = 58$ K is shown in Fig. 1. Figure 1(a) demonstrates that there is no significant oxygen loss until the temperature reaches 400 °C. There is also no observable feature below 400 °C that might be associated with the reported phase transition around 350 °C.⁸ The absence of significant weight loss in the 200 to 300 °C regime rules out appreciable water hydration into the sample. In Fig. 1(b), we present the weight loss as a function of time while the sample is held at 900 °C. The long flat tail after about 4 h (and exceeding beyond) marks the completion of the reduction process.

In the reduction of $Y_1Ba_2Cu_3O_{7-\delta}$, it has been the approach of several research groups^{2,20} to assume that Y_2O_3 , BaO, and pure Cu are the final products after reduction and that there is no loss of the metallic components. This suggests that the oxygen content per formula unit is 3.5 in the final-state powder. However, these assumptions are not valid for the La₁Ba₂Cu₃O_{7-\delta} system. A careful x-ray-diffraction analysis of our samples after hydrogen



FIG. 1. (a) The weight as a function of temperature for a sample with $T_c = 58$ K in an atmosphere of 95% N₂ and 5% H₂. A sharp drop in weight can be observed above 400 °C, approximately the maximum oxygen uptake temperature in the sample preparation process. (b) The weight loss of the same sample as a function of time. Note the difference in the weight scales between (a) and (b). The sample was held at 900 °C under the same reducing atmosphere as in (a). The reduction is nearly complete after about 260 min. The slight decrease in weight after this time is likely a result of the decomposition of La and Ba oxides. The slow change after 260 min introduces an uncertainty in determining the total weight loss.

reduction reveals the existence of the following components (in order of their abundance): Cu metal, BaO, LaCuO₂, BaCuO₂, Ba, La₂O₃, La, and CuO. The presence of so many phases makes simple assumptions about the oxygen content impossible and it is likely that such assumptions would overestimate the oxygen content. A failure of these assumptions in the Y-Ba-Cu-O system could possibly account for the discrepancy between the value of oxygen content determined by thermogravimetric analysis, and the value determined by neutron diffraction.²

To avoid this problem, we used a different approach. We assumed that the final oxygen content in all samples after the hydrogen reduction is the same. This is based on the fact that these samples were prepared from raw powders mixed according to the same stoichiometry. The difference in oxygen content and level of disorder causes different T_c 's for these samples. But after the reduction, the final oxygen content is determined by the amount of metallic components, independent of the initial oxygen content. Once we know the final oxygen content after the reduction, the initial oxygen content in the samples can be easily calculated from the weight loss. We used a control sample to determine the final oxygen content. This sample consisted of La₂O₃, BaCO₃, and CuO powders in amounts such that the initial La:Ba:Cu stoichiometry was 1:2:3. The powders had been prebaked at 110°C overnight to drive away any possible water, moisture, or other trapped gas. This prebake temperature was not high enough to decompose any of the constituent powders. After reduction, the weight loss was found to be 17.94% leading to a final oxygen content of 3.073 (taking into consideration CO_2 loss as well). The fact that this value was below the previously assumed value of 3.5 confirmed the x-ray observation that some of the Ba and La oxides were completely reduced.

The critical assumption that the final products after reduction (including the products of the control sample) have the same oxygen content has been tested by the xray-diffraction experiments. Powder x-ray-diffraction measurements were made on several samples with different T_c 's as well as the control sample after the reduction. In Fig. 2, we show two diffraction patterns obtained from the control sample (bottom pattern) and a real sample (top pattern). We can see that these patterns are all the same. This means the oxidation states of the metallic components in the final products are the same and therefore justifies the assumption that the oxygen content is the same after reduction.

In Fig. 3, we show the variation in T_c as a function of oxygen content in the La₁Ba₂Cu₃O_{7- δ} system. The sample with the highest T_c (72 K) had an oxygen content of 6.75. As the oxygen content is reduced from this value, the transition temperature decreases smoothly to 44 K. This result agrees with the T_c -oxygen-content behavior observed in the orthorhombic Y₁Ba₂Cu₃O_{7- δ} compound in which T_c increases with increasing oxygen occupancy in the Cu-O chains.¹⁸ However in the La₁Ba₂Cu₃O_{7- δ} system, as the oxygen content is increased from the value of 6.75 to a value near 7.25, T_c decreases from 72 to 23 K. To explain these results, we suggest the following picture.

FIG. 2. The x-ray-diffraction patterns of the control sample (bottom curve) and a real sample (top curve). Both of these patterns were obtained immediately after the reduction process is finished. The similarity between these diffraction patterns means that the oxidation states of the metallic components in the final products are the same and therefore justifies the assumption that the oxygen content is the same for all the samples after reduction.

(i) Starting from the peak value of $T_c = 72$ K, as oxygen is removed from the b axis in the outer Cu-O planes where ordered Cu-O chains are present, the resulting oxygen disorder reduces T_c to the value of 44 K (and then presumably to zero). (ii) As more oxygen is incorporated into the vacant sites on the *a* axis in the outer Cu-O planes, leading to an increase in the oxygen content and a further interruption of the ordered Cu-O chain formation, T_c is also reduced. These suggestions are consistent with the fact, that, for a perfect one-dimensional Cu-O chain structure along the b axis, the oxygen content is 7 and that some vacant oxygen sites on the *a* axis have to be filled when the oxygen content is larger than 7. The orthorhombic distortion associated with the Cu-O chains is reduced when the vacant oxygen sites on the *a* axis are partially populated. We note that even if the a and b lattice constants are equal, it is still possible that the chains are not totally destroyed and the structure is still considered to have orthorhombic symmetry. Refined neutron data on these relatively low T_c samples should be able to resolve this point.

The complicated dependence of T_c on the oxygen content may be associated with lanthanum-barium disorder. This disorder is associated with the substitution of some La³⁺ ions into the Ba²⁺ sites and vice versa. The La³⁺ ion with radius r=1.15 Å is similar to that of the Ba²⁺ ion with radius r=1.35 Å in terms of ionic radius and atomic weight and electronic structure. This similarity is the reason why La-Ba disorder can be easily developed. Disorder of this type has been observed in Y₁Ba₂Cu₃-O_{7- δ}.²¹ However, in this latter case, the magnitude of the disorder would not be expected to be large since the Ba²⁺ ion (r=1.35 Å) and the Y³⁺ ion (r=0.93 Å) have quite different radii. Since local charge neutrality requires that the La³⁺ ions draw in more negative oxygen ions than the

FIG. 3. The zero-resistance temperature T_c as a function of the oxygen content in the original samples. The squares are the data points from this study while the diamonds are data taken on Y-Ba-Cu-O and reported in Ref. 18. The solid line is a guide for the eye. The error bars were dictated by (i) the uncertainty in determining the total weight loss of each sample as shown in Fig. 1(b) and (ii) the possible variation of the final oxygen content (namely the deviation from the value 3.073).

 Ba^{2+} ions, more oxygen ions are then trapped into these sectors. On the other hand, the substitution of the Ba on the central La sites has little consequence on the oxygen content since the oxygen in this layer was totally absent to begin with. The only probable effect is the reduction of the dimpled structure of the inner Cu-O planes that sandwich the central La site. We therefore propose that the disorder between the La³⁺ ions and the Ba²⁺ ions causes additional oxygen occupancy in the otherwise vacant sites on the *a* axis. This additional oxygen occupancy interrupts the Cu-O chain formation, leading to severe reduction in the superconducting transition temperature.

We would like to focus on the differences between the La system and the Y system. In the Y system, the disorder is essentially associated with the oxygen vacancies. The yttrium ions are quite different from the barium ions and the disorder between these ions is not of major concern. Therefore, the degree of disorder in the yttrium system is uniquely associated with the oxygen content: higher oxygen content always corresponds to increased order. However, in the lanthanum system, this is not true. The disorder between the lanthanum ions and the barium ions makes possible an extra oxygen occupancy and thus the oxygen content is not the only indicator of degree of disorder.

Our recent neutron diffraction experiment shows increasing disorder in samples with decreasing T_c 's.^{9,10} The temperature dependence of resistivity also shows an increase in the magnitude of resistivity at room temperature, when the superconducting transition temperature of the samples progressively decreases. These observations strongly suggest that the degree of disorder is greatly





enhanced in the samples with low superconducting transition temperatures.

In the La-Ba-Cu-O series, the $La_{3-x}Ba_{3+x}Cu_6O_{14+y}$ (Ref. 22) phase cannot be distinguished from the La_1Ba_2 - $Cu_3O_{7-\delta}$ phase by x-ray diffraction due to the similar scattering of the isoelectronic La^{3+} and Ba^{2+} ions and the comparably low scattering of the oxygen atoms in the structure. We know of several investigations into the relationship of T_c to the La doping range between the 3:3:6 phase and the 1:2:3 phase in an attempt to determine if the 3:3:6 phase is superconducting, and likewise, whether a tetragonal structure could be associated with the acquisition of very high T_c 's.¹¹⁻¹⁶ Preliminary neutron data have already strongly indicated that the 3:3:6 oxygen configuration is minimal to nonexistent in the La₁Ba₂- $Cu_3O_{7-\delta}$ compound.^{9,10} It would seem that the doping of La onto the Ba sites would have similar results to the effects of La-Ba disorder in undoped La₁Ba₂Cu₃O_{7- δ}. Recent reports indicate this to be true.^{11,12} However, unless an accurate refinement of neutron data in the La-

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doping investigations is performed, the extra effect of lanthanum-barium disorder will be another variable to consider.

In conclusion, we have performed systematic TGA measurements on a series of $La_1Ba_2Cu_3O_{7-\delta}$ samples with zero resistance T_c 's ranging between 23 and 72 K. Our results demonstrate extra oxygen content in samples with T_c 's below 44 K. This behavior can be explained by the disorder of La and Ba ions, which leads to the disruption of the Cu-O chain formation in the outer Cu-O planes. Our results for the samples with T_c 's greater than 44 K are in good agreement with the observations of others¹⁸ for $Y_1Ba_2Cu_3O_{7-\delta}$.

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