Hole filling and hole creation in the superconducting compounds Bi$_2$Sr$_{2-x}$R$_x$CuO$_{6+y}$ (R = La, Pr, Nd, and Sm)

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The superconducting properties, hole content, and lattice constants of several rare-earth-doped compounds Bi$_2$Sr$_{2-x}$R$_x$CuO$_{6+y}$ have been investigated as a function of rare-earth doping and oxygen content. The maximum superconducting transition temperature, T_c, obtained for each of the rare-earth dopants was 23 K (La), 25 K (Pr), 21 K (Nd), and 12 K (Sm). The T_c's of these compounds exhibited a parabolic dependence on the La and Pr concentration ($0 < x < 1$), with the maximum T_c occurring for $x = 0.4$ for samples with low oxygen content. For La- and Pr-doped samples treated in pure oxygen, the position of the maximum shifted to $x = 0.6$ and 0.5, respectively, with a concurrent reduction in the maximum value for T_c (17 K for La and 18 K for Pr). For $x > 0.2$, the samples were single phase and exhibited unusually sharp superconducting transitions (width of ac-susceptibility transition less than 2 K). The high quality of the samples allowed a precise study of the variation of the orthorhombic cell parameters with the rare-earth and oxygen content. The oxygen content of the samples was systematically varied using oxygen partial pressures that ranged from 100 ppm to 100% oxygen during the heat treatments. Absolute values of the oxygen content and the changes of the oxygen content with heat treatments were determined using thermogravimetric analysis. The qualitative features of the dependence of T_c on x and y can be understood by assuming an excess of holes in the Cu-O planes of the undoped compound that are filled by the extra electrons contributed with rare-earth doping or increased with the addition of oxygen. For La-doped samples treated in pure oxygen there was a smooth variation of T_c with hole content, with the maximum T_c (18 K) occurring at a hole content of 0.2±0.02. For La-doped samples treated in 0.1% oxygen, the maximum T_c occurred at the same hole content (0.2), but the value of T_c was significantly higher (23 K). These data illustrate that, even within one alloy system, composition can affect T_c as well as hole content. Finally, lattice-constant and oxygen-content data from the Pr-doped materials suggest that Pr substituted onto the Sr site has a formal valence of approximately 3.3.

I. INTRODUCTION

The compound Bi$_2$Sr$_2$CuO$_6$ (Ref. 1) is one of a large family of superconducting compounds (BiO)$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2}$ ($n = 1, 2, 3$) (Refs. 2–4) and (TlO)$_2$Ba$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2}$ ($n = 1, 2, 3$).[5–7] Although initially Bi$_2$Sr$_2$CuO$_6$ appeared to be the simplest of the Bi cuprates, further work on this compound has demonstrated several unusual characteristics that have severely hampered research efforts. The formal composition "Bi$_2$Sr$_2$CuO$_6$" (also termed the 2:2:0:1 phase), which was based on early x-ray structure refinements,[3] is not found either in single crystals or ceramics. Several studies[8–10] of the Bi$_2$O$_3$-SrO-CuO phase diagram have shown that, at the 2:2:0:1 composition, the equilibrium phase that forms is not the original superconducting phase discovered by Raveau and co-workers[1] but is a distinct layered ternary compound with a 1-Å smaller stacking repeat distance ($c = 23.6$ Å). This layered phase is semiconducting, not superconducting, and will be referred to as the "collapsed phase."[11] Single-phase or nearly single-phase ceramics of the Raveau phase ($c = 24.6$ Å) can be prepared either with a Sr deficiency or with both a Bi excess and a Sr deficiency,[8,12] but none of these "single-phase" ceramics

are superconducting. Interestingly, it is possible to prepare superconducting single crystals from the melt that are only slightly deficient in Sr. The crystals, however, appear to be metastable and partially decompose with fairly mild heat treatments (600 °C oxygen).[13] The lack of stability of this phase coupled with a superstructure modulation that varies with the Sr deficiency[14] has made it very difficult to investigate the superconducting characteristics of this material.

The substitution of various rare earths (primarily La) for Sr in the 2:2:0:1 phase was previously investigated by several workers.[15,16] All found an enhancement in the superconducting transition temperature with rare-earth doping although, in much of the early work, the samples clearly were not single phase. More recently, it has been shown that single-phase samples exist in the Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+y}$ system for $0.2 < x < 1.2$, and that a maximum T_c of about 25 K is attained for $x = 0.4$.[17,18] Analysis of the carrier concentration for this family of materials has shown that one can consider the substitution of La^{3+} for Sr^{2+} as filling the excess holes and thus attaining the maximum T_c by tuning the hole concentration to an optimum value of about 0.2 holes per Cu-O unit.[19,20] As has been observed in other superconducting

cuprate compounds, T_c decreases if the hole concentration is much higher or lower than the optimum value.[21-23]

The purpose of the present work was to investigate the variation of the lattice constants, T_c, and the carrier concentration with both the R concentration x and various annealing atmospheres (100 ppm to 1 atom O_2) for the compounds $Bi_2Sr_{2-x}R_xCuO_{6+y}$, where R = La, Ce, Pr, Nd, Sm, Eu, and Gd. Of particular interest in the present study were the variation of oxygen content y with different heat treatments, the thermal stability of these materials, and the possible effects of a mixed Pr valence (i.e., a valence between 3 and 4) on the superconductivity of these materials.

II. EXPERIMENT

Ceramics of $Bi_2Sr_{2-x}R_xCuO_{6+y}$, R = La, Ce, Pr, Nd, Sm, Eu, and Gd, were prepared from stoichiometric quantities of high-purity Bi_2O_3, $SrCO_3$, CuO and rare-earth oxides that were predried at temperatures of 300–1000 °C prior to weighing. Approximately 5-gm batches of material were thoroughly ground together and pressed into pellets using a pressure of about 1000 kg/cm². The pellets were fired for 16 h in air at 740, 780, 810, 830, and 860 °C on gold foil. Between each firing the pellets were reground and repressed. The incorporation of the rare earths for Sr in the 2:2:0:1 phase was somewhat sluggish but was enhanced by reacting the material in pellet form. Prior to the final firing, several small pellets (3 mm diam × 5 mm high) were pressed at approximately 2500 kg/cm². The final density of the ceramics depended primarily on the pressure applied prior to firing rather than the firing temperature.

X-ray powder diffraction was performed using a SCINTAG automated diffractometer with a solid-state Ge detector using Cu $K\alpha$ radiation. Reported cell parameters were derived from peak positions corrected for instrumental errors with respect to the National Bureau of Standards (NBS) standard Si 640b. For each pattern, 6–13 resolvable peaks were indexed using an orthorhombic cell and the cell dimensions were estimated by the least-squares method.

The superconducting transition temperature of each sample was determined by measuring the ac magnetic susceptibility from room temperature to 4.2 K. Temperature was determined using a calibrated Si diode placed next to the sample. Unless otherwise stated in the text, the transition temperature was defined to be the temperature at which the magnetic transition was 10% complete. For a few samples, resistivity measurements were made using standard four-probe techniques with a dc current of 3 mA, the polarity of which was alternated approximately twice a sec.

Thermogravimetric (TGA) measurements were made on selected ceramic samples using a Perkin-Elmer TGS-2 system. These measurements were used to determine the changes in oxygen content of the ceramics after heat treatments in various oxygen partial pressures. The oxygen partial pressures in the various gas cylinders used were independently checked using an Ametek S-3a

zirconia-based oxygen sensor. The absolute oxygen contents of the ceramics were determined by hydrogen reduction in the TGA system using a gas mixture of 4% H_2 and 96% argon.

A standard heating protocol was used for modifying the oxygen content of the samples. The ceramics were heated to 750 °C at a rate of 10 °C/min, held at 750 °C for 16 h, and then cooled to room temperature at 10 °C/min. This heating protocol produced magnetic superconducting transitions that were narrow (10–90 % transitions of 2–3 K) for all oxygen partial pressures studied (100 ppm to 100% oxygen). Samples treated using this heating procedure showed no evidence of degradation or phase decomposition (unlike the undoped 2:2:0:1 ceramics and crystals studied previously[8,13]). The same heat treatment could be easily reproduced in both the TGA apparatus and in a controlled-atmosphere tube furnace, thus making it possible to directly correlate the superconducting properties of samples treated either in the TGA apparatus or the tube furnace.

III. RESULTS AND DISCUSSION

A. Cell parameters and phase purity

Of the rare-earth dopants, La and Pr were investigated in the most detail. Ceramic samples of $Bi_2Sr_{2-x}R_xCuO_{6+y}$, R = La, Pr, were prepared with x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 as described above. A careful analysis of the x-ray-diffraction patterns indicated that, with La doping, the samples were single phase for $x > 0.3$, and for Pr doping the range was $0.2 < x < 0.9$. For x values of 0.3 and lower, the phase assemblage consists of the "collapsed phase" and the Raveau phase with the relative amount of the collapsed phase increasing with decreasing x. At x = 0 the relative amounts of the two phases are about equal on the basis of the relative intensity ratios of the most intense x-ray-diffraction peaks. Considering the trends of the cell-dimension variations (Figs. 1 and 2), the cell dimensions of the Raveau phase at low x indicate a higher rare-earth content than expected for a single-phase sample. This suggests that the La and Pr preferentially partition into the Raveau phase over the "collapsed phase." For both sets of samples, the 2:2:0:1 phase orthorhombic cell parameters followed similar trends. The a and b cell dimensions increased (about 1%) with rare-earth doping while the c dimension decreased (about 2.5%) with rare-earth doping (see Figs. 1 and 2). The decrease in c with increasing R content is explained primarily by the substitution of the smaller R ion for the larger Sr. The smaller increase in a and b with increasing R content is probably caused by the reduced formal valence of Cu which shortens the Cu—O bonds, and by the added oxygen which is accommodated in the Bi_2O_2 slab of the structure. By analogy to the structural models for $Bi_2Sr_2CaCu_2O_{8+y}$,[24] which has a similar Bi_2O_2 slab, the increased occupation of the disordered oxygen sites will have a greater effect on a and b than c.

For the other rare earths investigated (Ce, Nd, Sm, Eu, and Gd), only samples with x = 0.4 were prepared be-
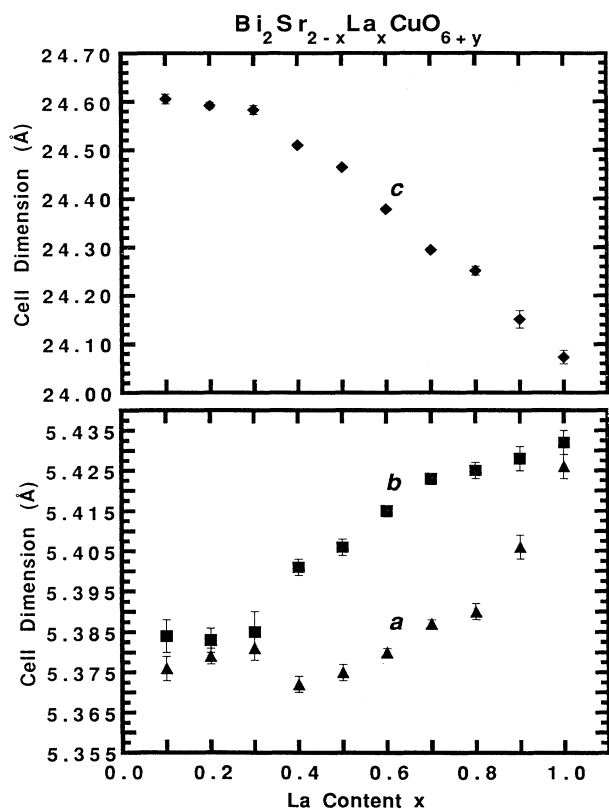
FIG. 1. Variation of the orthorhombic unit-cell dimensions of $Bi_2Sr_{2-x}La_xCuO_{6+y}$ with La content x.
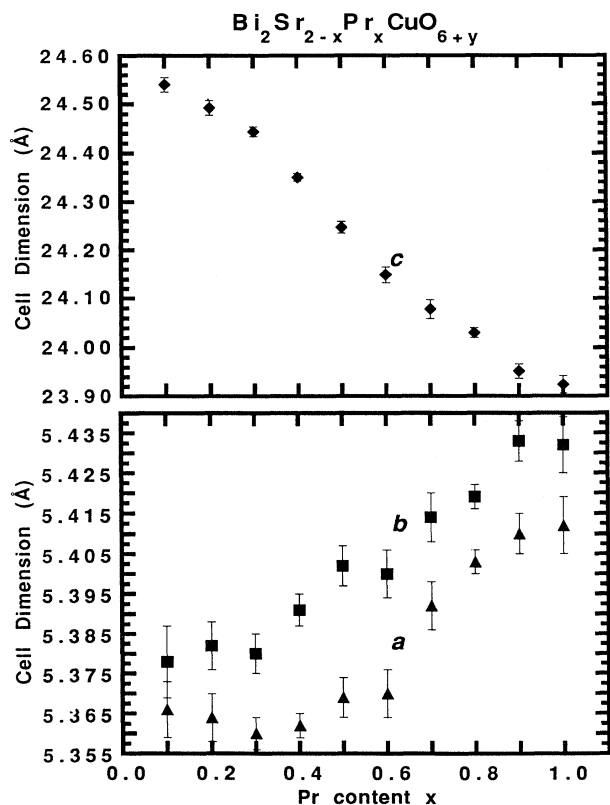

FIG. 2. Variation of the orthorhombic unit-cell dimensions of $Bi_2Sr_{2-x}Pr_xCuO_{6+y}$ with Pr content x.

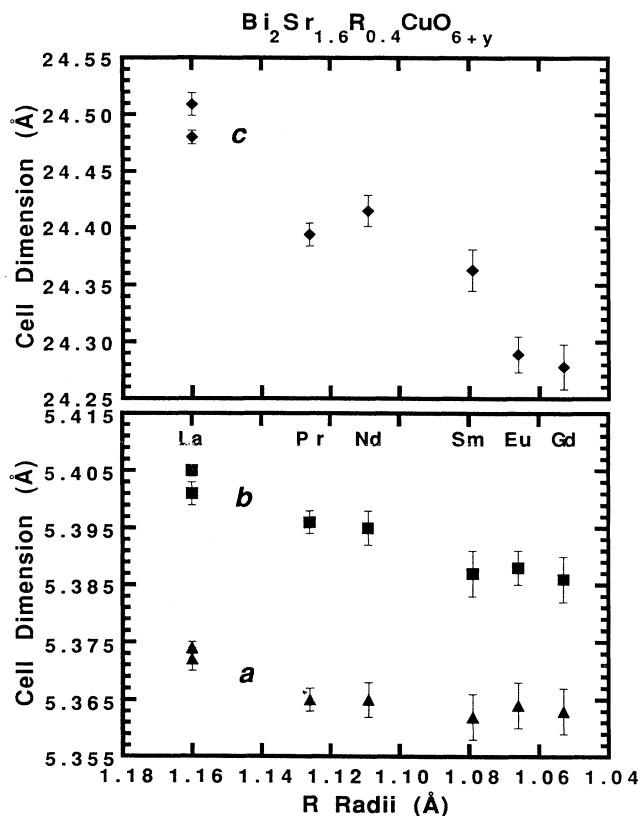FIG. 3. Variation of the orthorhombic unit-cell dimensions of $Bi_2Sr_{1.6}R_{0.4}CuO_{6+y}$ with rare-earth dopant (La, Pr, Nd, Sm, Eu, Gd). Note the deviation of the value of the Pr c unit-cell dimension from the trend established by La and Nd. These data suggest an intermediate valence for Pr in this compound.

cause, in the case of La and Pr, this doping level resulted in the maximum T_c. It was found that Ce would not substitute for Sr in the 2:2:0:1 phase presumably because the Ce valence is near 4. With Nd and Sm the samples were single phase, but for Eu and Gd a small amount of an unidentified impurity phase was also present, indicating that the smaller rare-earth ions (Eu and Gd) are not easily accommodated on the Sr site. The variation of the orthorhombic cell parameters with rare-earth dopant ($x = 0.4$) is shown in Fig. 3. An interesting observation is the deviation of the c cell dimension for Pr from the trend established by the other rare earths suggesting an intermediate valence for Pr between 3 and 4. This type of lattice constant versus the rare-earth plot is a standard way of identifying rare-earth ions with an intermediate valence.[25,26] A more quantitative estimate of the Pr valence in the 2:2:0:1 phase will be given below.

B. Superconducting properties

The superconducting transition temperatures of $Bi_2Sr_{2-x}La_xCuO_{6+y}$ samples, as determined from magnetic ac susceptibility measurements, are plotted in Fig. 4 versus the La content x for samples heated at 750 °C in either 0.1% or 100% oxygen. For both heat treatments,
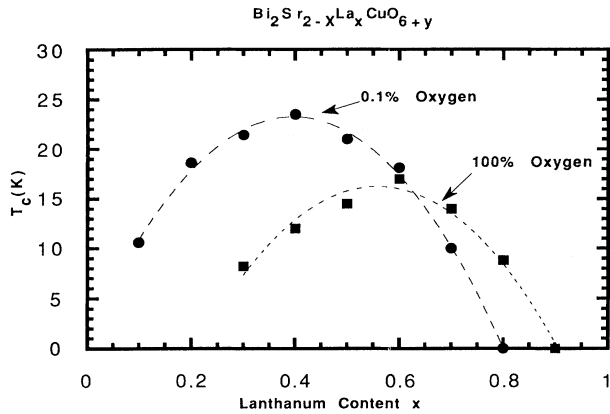
$Bi_2Sr_{2-x}La_xCuO_{6+y}$

FIG. 4. Superconducting transition temperature (10% magnetic) vs La content for $Bi_2Sr_{2-x}La_xCuO_{6+y}$ samples treated at 750 °C in either 0.1% oxygen (●) or 100% oxygen (■).
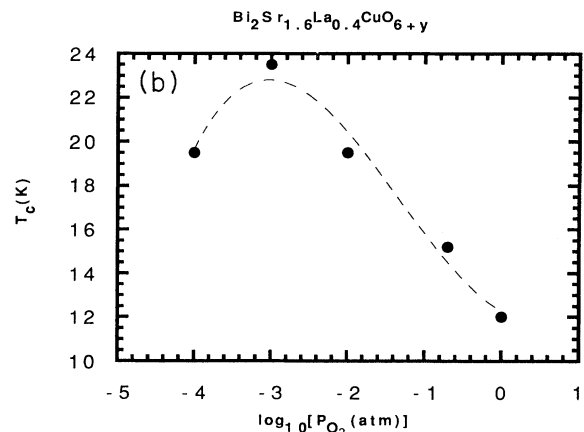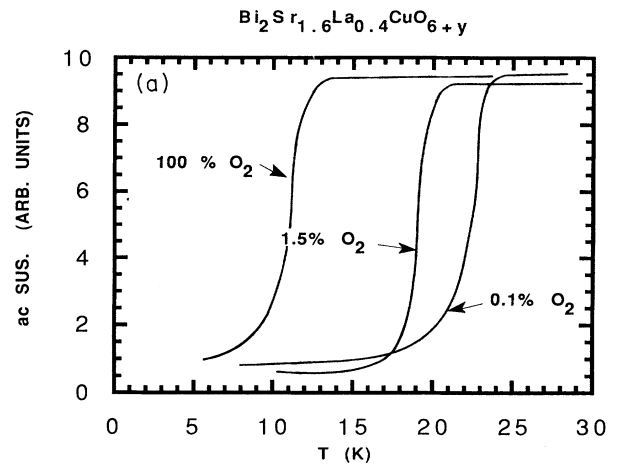
$Bi_2Sr_{1.6}La_{0.4}CuO_{6+y}$

$Bi_2Sr_{1.6}La_{0.4}CuO_{6+y}$

FIG. 5. (a) ac magnetic susceptibility traces for a $Bi_2Sr_{1.6}La_{0.4}CuO_{6+y}$ sample that was heated in different partial pressures of oxygen. (b) The variation of T_c with the log of the oxygen partial pressure for the same sample.

T_c has roughly a parabolic dependence on the La content (as indicated in the figure by the dashed lines). The parabolas, however, are displaced with respect to each other with the maximum T_c (23 K) for samples treated in 0.1% oxygen occurring at a La content of 0.4, whereas for samples treated in pure oxygen, the maximum T_c (17 K) occurs at a La content of 0.6. For a given La content the change in oxygen content y induced by the different heat treatments can result in a substantial change in T_c. For example, at $x = 0.3$, T_c changes from 21 to 8 K for heat treatments in 0.1 and 100 % oxygen, respectively. If the superconducting transition temperature was less than 4.2 K, these data were plotted in the figure with a transition of 0 K.

ac susceptibility traces for a $Bi_2Sr_{1.6}La_{0.4}CuO_{6+y}$ sample that was heated in different oxygen partial pressures are shown in Fig. 5. The traces all indicate approximately the same degree of magnetic shielding and all are approximately 2 K in width (10–90 %) indicating relatively uniform oxygen content. However, if following the heat treatment at 750 °C the ceramics were quenched to room temperature rather than cooled at 10 °C/min, the superconducting transition became substantially broader, > 6 K. A typical resistivity curve for a $Bi_2Sr_{1.6}La_{0.4}CuO_{6.3}$ ceramic is shown in Fig. 6.

The T_c versus x behavior for the Pr-doped $Bi_2Sr_{2-x}Pr_xCuO_{6+y}$ samples (Fig. 7) is similar to that found with La doping. The only qualitative difference between the Pr and La T_c data is that the T_c versus x parabolas are more highly peaked for the Pr data. This feature is probably related to a more limited solubility limit of Pr for Sr in the 2:2:0:1 structure. For the Pr-doped materials, the maximum T_c (25 K) for samples treated in 0.1% oxygen occurs at $x = 0.4$, just as was the case for La, but in pure oxygen the maximum T_c (18 K) is only shifted to $x = 0.5$.

The variation of T_c with rare-earth dopant is shown in Fig. 8 for compounds with the composition $Bi_2Sr_{1.6}R_{0.4}CuO_{6+y}$ where $R =$ La, Pr, Nd, Sm, Eu, and Gd. The optimum oxygen content for these samples (i.e.,

$Bi_2Sr_{1.6}La_{0.4}CuO_{6.30}$
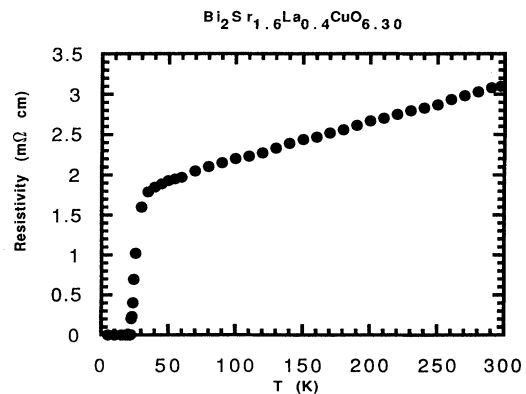
FIG. 6. Resistivity vs temperature for $Bi_2Sr_{1.6}La_{0.4}CuO_{6.30}$.
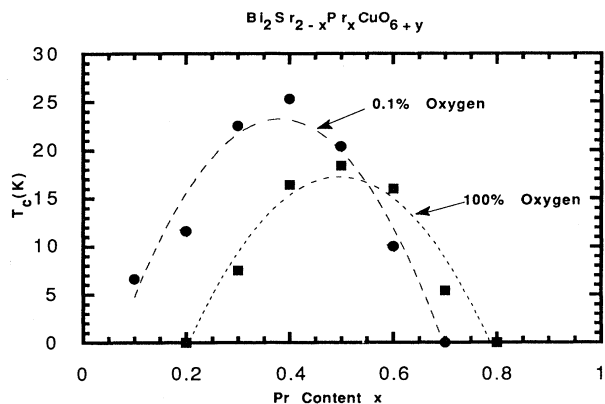
FIG. 7. Superconducting transition temperature (10% magnetic) vs Pr content for $Bi_2Sr_{2-x}Pr_xCuO_{6+y}$ samples treated at 750 °C in either 0.1% oxygen ($\bullet$) or 100% oxygen ($\blacksquare$).

maximum T_c) was attained by heating the samples at 750 °C in 0.1% oxygen followed by cooling to room temperature at 10 °C/min. As noted above, Ce would not substitute for Sr in these materials. The decrease in T_c for the heavier rare earths is probably due to the increasing mismatch between the Sr and rare-earth ionic radii caused by the lanthanide contraction. Also, for R's heavier than Nd, the extent of R substitution for Sr in the 2:2:0:1 phase decreases.

C. Oxygen content

Both the change in oxygen content with oxygen partial pressure and the total oxygen content were determined for several of the La- and one of the Pr-doped samples using thermogravimetric analysis. The samples were first heated in pure oxygen in the TGA system to 750 °C at 10 °C/min, held for 16 h, then cooled to room tempera-

ture at 10 °C/min. This removed any adsorbed water or CO_2 from the samples and provided a reference starting weight for which the T_c was known. While still in the TGA system, the partial pressure of oxygen was reduced to either 100 ppm (0.01%) or 1000 ppm (0.1%) and the samples were subjected to the same standard heat treatment (750 °C for 16 h, cooled at 10 °C/min). The change in weight from the fully oxygenated sample to the same sample treated in a low-oxygen partial pressure was converted to a change in oxygen content y. In going from 100% oxygen to 0.1% oxygen, the change in y was 0.035 ± 0.005, while in going from 100% oxygen to 0.01% oxygen the change in y was 0.065 ± 0.005, and within the stated error bars was independent of the La content. After the heat treatment of the sample in a low-oxygen partial pressure, the gas composition was changed to a mixture of 4% H_2-96% Ar without removing the sample from the TGA system. Slowly heating (5 °C/min) the sample in this gas composition reduced the sample to Bi metal, Cu metal, SrO and either La_2O_3 or Pr_2O_3. The hydrogen reduction of the samples was complete at temperatures between 600 and 650 °C. It was initially not certain that this reduction would result in Pr_2O_3, so the same reduction treatment was applied to the Pr oxide that is stable under ambient conditions (Pr_6O_{11}). TGA and x-ray analysis of the reduced material indicated that Pr_2O_3 was indeed formed.

The total oxygen content z of several of the La-doped 2:2:0:1 samples is shown in Fig. 9 after heat treatments in either 100% oxygen or 0.01% oxygen. As La is substituted for Sr in $Bi_2Sr_{2-x}La_xCuO_{6+y}$, oxygen is also added to the structure so that one La atom only fills part of one hole. Assuming a valence of $+2$ for Sr and $+3$ for La and Bi, the hole concentration in the Cu-O plane is simply given by $2y - x$.

The superconducting transition temperatures versus hole concentration are shown in Fig. 10 for La-doped samples treated either in 0.1% oxygen or 100% oxygen. The error bars shown in the figure represent the estimated error in determining the oxygen content. For the La-
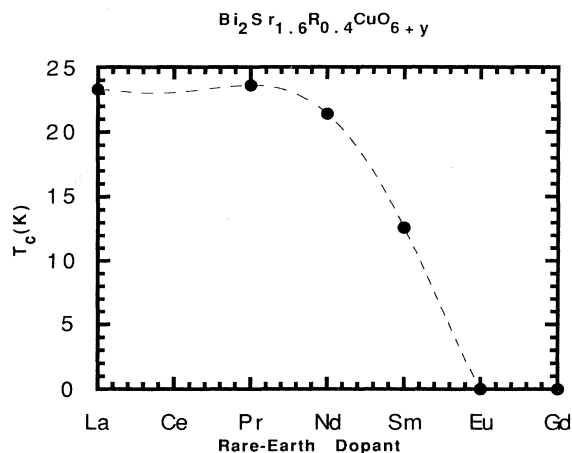

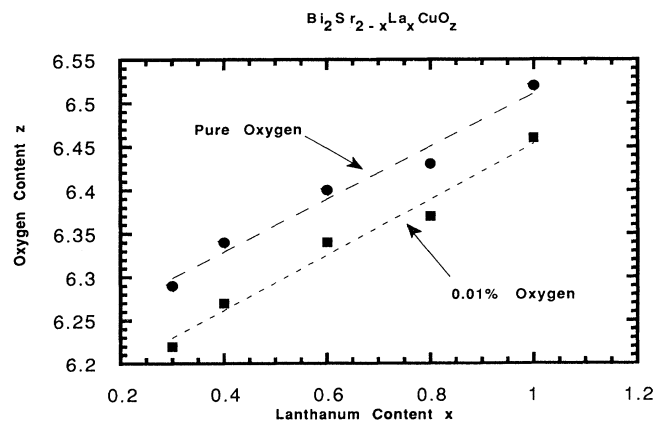FIG. 8. Superconducting transition temperature vs R dopant for $Bi_2Sr_{1.6}R_{0.4}CuO_{6+y}$ samples.

FIG. 9. Total oxygen content z vs La content x for $Bi_2Sr_{2-x}La_xCuO_z$ samples treated at 750 °C in either 0.01% oxygen ($\blacksquare$) or 100% oxygen ($\bullet$).
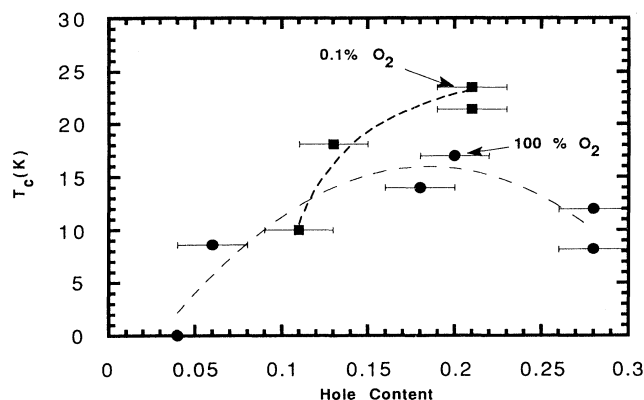
FIG. 10. Superconducting transition temperature vs hole content for $Bi_2Sr_{2-x}La_xCuO_{6+y}$ samples treated at 750 °C in either 0.1% oxygen (■) or 100% oxygen (●).

doped samples treated in pure oxygen, the data fall on a smooth curve (dashed line in Fig. 10) that peaks at a hole concentration near 0.2 for which the maximum T_c is about 17 K. For the same samples treated in 0.1% oxygen, however, only the lower half of the hole concentration versus the T_c curve is attainable, but the maximum also appears to occur near a hole concentration of 0.2.

The correlation between T_c and hole content has been observed previously in the $Bi_2Sr_2CaCuO_{8+y}$ (Ref. 23) and $Bi_2Sr_2CuO_{6+y}$ (Refs. 19 and 20) systems and in several of the other superconducting systems that have Cu-O planes such as $La_{2-x}Sr_xCuO_4$ (Ref. 21) and $YBa_2Cu_3O_y$.[22] In the present work the maximum T_c for the $Bi_2Sr_{2-x}La_xCuO_{6+y}$ system occurs at a hole content of 0.2, a value that is between the value of 0.12 found by Maeda et al.[20] and the value of 0.3 reported by Groen et al.[19] These workers, however, determined the oxygen content of their samples using an iodometric titration technique rather than the hydrogen reduction technique employed here. Although, in principle, these two techniques have similar levels of accuracy, the hydrogen reduction technique is less prone to complications associated with an uncertain Bi valence in solution. An additional determination of the oxygen content of these same materials was also reported by Bauhofer et al.,[27] but their data are in qualitative disagreement with the data of Maeda et al.,[20] Groen et al.,[19] and the present work.

Two different La-doped samples have (within experimental error) the same optimum hole concentration of 0.2. In one case the optimum hole content is attained with a La content of 0.4 and a treatment in 0.1% oxygen, whereas in the other case it is obtained with a La content of 0.6 and a treatment in 100% oxygen. Since the T_c's of the two samples are significantly different (17 versus 23 K), these data illustrate that, even within a given alloy system, T_c can be affected by composition as well as by hole concentration. A structural refinement of both of these samples is currently in progress to see if the higher T_c correlates with a greater tendency of the holes to re-

side on the oxygen ion. Correlations between various bond valence sums and T_c recently have been demonstrated by Tallon[28] and by Whangboo and Toradi;[29] it will be interesting to test the generality and fundamental basis of these correlations.

The oxygen content of a $Bi_2Sr_{1.6}Pr_{0.4}CuO_{6+y}$ sample was determined as described above. The total oxygen content found for this sample treated in 0.1% oxygen was 6.36 ± 0.01. This sample had the maximum T_c of 25 K for this family of compounds, and hence it seems reasonable to assume that the optimum hole concentration should be 0.2, the same as for the La-doped samples. If the Pr valence were 3, then the hole concentration would be 0.3 rather than 0.2 This difference can be accounted for if the Pr valence in these materials is about 3.3. The x-ray data shown in Fig. 3 are also qualitatively consistent with an intermediate value for the Pr valence.

It has been previously noted[30] that $PrBa_2Cu_3O_7$ forms with the same structure as the other "1:2:3" superconducting materials, yet does not exhibit any evidence of superconductivity. The puzzling lack of superconductivity in this material has provided an indirect means of probing the nature of superconductivity in the other "1:2:3" materials. The several possible reasons proposed for the lack of superconductivity in this material have included a Pr valence near $4+$ (or significantly greater than $3+$) and a filling of the mobile holes in the adjacent Cu-O planes,[31,32] strong magnetic scattering (pair breaking) caused by a mixed Pr valence and the resulting strong hybridization between the conduction electrons and the Pr $4f$ electrons,[31,33] and a small concentration of Pr^{4+} ions substituting for Cu.[34] Although the Pr sites in the "1:2:3" structure and in the 2:2:0:1 structure are not identical, one might expect the physical effect of the Pr to be similar in both materials. In the 2:2:0:1 materials, the Pr valence clearly appears to be intermediate (3.3) so that one would expect a large degree of hybridization between the $4f$ and the conduction electrons. In the 2:2:0:1 materials, however, this hybridization does not seem to affect T_c to any measureable degree since the T_c of the Pr-doped compound is just as high as (actually slightly higher than) that found for the La-doped 2:2:0:1 materials. The role of Pr in the 2:2:0:1 materials appears to be the same as La; that is, it fills the excess mobile holes in the Cu-O planes. The lack of any depression of T_c when La is replaced by Pr also suggests that, in the 2:2:0:1 materials, Pr does not substitute for Cu. These results indirectly suggest that the absence of superconductivity in $PrBa_2Cu_3O_7$ is mostly due to hole filling by the extra electrons contributed by Pr. Recent magnetic penetration depth studies on $Y_{1-x}Pr_xBa_2Cu_3O_7$ alloys also suggest that hole filling is the dominant mechanism for T_c suppression.[32]

IV. CONCLUSIONS

(1) For $Bi_2Sr_{2-x}R_xCuO_{6+y}$, $R = La$, Pr, the hole concentration and, hence, the superconducting properties, can be varied either by increasing the rare-earth-doping level, which reduces the number of mobile holes, or by heat treatment in higher-oxygen partial pressures which

increases the number of mobile holes. The optimum hole concentration to maximize T_c for these materials is about 0.2 holes per Cu-O layer.

(2) Even within a family of compounds, $Bi_2Sr_{2-x}La_xCuO_{6+y}$, the superconducting transition temperature can be affected by composition as well as by hole concentration.

(3) For $Bi_2Sr_{2-x}Pr_xCuO_{6+y}$ alloys, the Pr valence as determined by oxygen content and x-ray measurements is about 3.3.

(4) The effect of Pr on the superconducting 2:2:0:1 materials can be explained using only a "hole-filling" argument. No evidence of magnetic pair breaking, or of suppression of T_c due to hybridization between the $4f$ and conduction electrons, is observed.

ACKNOWLEDGMENTS

[1]C. Michel, M. Hervieu, M. M. Borel, A. Grandin, F. Deslandes, J. Provost, and B. Raveau, Z. Phys. B **68**, 421 (1987).

[2]A. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, Jpn. J. Appl. Phys. **27**, L209 (1988).

[3]C. C. Torardi, M. A. Subramanian, J. C. Calabrese, J. Gopalakrishnan, E. M. McCarron, K. J. Morrissey, T. R. Askew, R. B. Flippen, U. Chowdhry, and A. W. Sleight, Phys. Rev. B **38**, 225 (1988).

[4]J. M. Tarascon, W. R. McKinnon, P. Barboux, D. M. Hwang, B. G. Bagley, L. H. Greene, G. W. Hull, Y. LePage, N. Stoffel, and M. Giroud, Phys. Rev. B **38**, 8885 (1988).

[5]Z. Z. Sheng and A. M. Hermann, Nature **332**, 55 (1988); **332**, 138 (1988).

[6]R. M. Hazen, L. W. Finger, R. J. Angel, C. T. Prewitt, N. L. Roos, G. G. Hadidiacos, P. J. Heaney, D. R. Veblen, Z. Z. Sheng, and A. M. Hermann, Phys. Rev. Lett. **60**, 1657 (1988).

[7]S. P. Parkin, V. Y. Lee, A. I. Nazzal, R. Savoy, R. Beyers, and S. J. La Placa, Phys. Rev. Lett. **61**, 750 (1988).

[8]B. C. Chakoumakos, P. S. Ebey, B. C. Sales, and Edward Sonder, J. Mater. Res. **4**, 767 (1989).

[9]J. A. Saggio, K. Sugata, J. Hahn, S. J. Hwu, K. R. Poeppelmeier, and T. O. Mason, J. Am. Ceram. Soc. **72**, 849 (1989).

[10]R. S. Roth, C. J. Rawn, and L. A. Bendersky, J. Mater. Res. **5**, 46 (1990).

[11]B. C. Chakoumakos, Edward Sonder, and B. C. Sales, in *High Temperature Superconductors: Fundamental Properties and Novel Materials Processing*, edited by D. K. Christen, J. Narayan, and L. F. Schneemeyer, MRS Symposia Proceedings No. 169 (Materials Research Society, Pittsburgh, 1990), p. 103.

[12]Edward Sonder, B. C. Chakoumakos, and B. C. Sales, Phys. Rev. B **40**, 6872 (1989).

[13]B. C. Sales, Edward Sonder, and B. C. Chakoumakos, in *High Temperature Superconductors: Fundamental Properties and Novel Materials Processing*, edited by D. K. Christen, J. Nayaran, and L. F. Scheenmeyer, MRS Symposia Proceedings No. 169 (Materials Research Society, Pittsburgh, 1990), p. 99.

[14]B. C. Chakoumakos, J. D. Budai, B. C. Sales, and Edward Sonder, in *High Temperature Superconductors: Relationships Between Properties, Structure and Solid State Chemistry*, edited by J. B. Torrance, K. Kitazawa, J. M. Tarascon, J. R. Jorgenson, and J. M. Thompson, MRS Symposia Proceedings No. 156 (Materials Research Society, Pittsburgh, 1989), p.

329.

[15]T. Den. A. Yamazaki, and J. Akimitsu, Jpn. J. Appl. Phys. **27**, L1620 (1988).

[16]M. Onoda, M. Sera, K. Fukuda, S. Kondoh, and M. Sato, Solid State Commun. **66**, 189 (1988).

[17]W. A. Groen, D. M. de Leeuw, and G. M. Stollman, Solid State Commun. **72**, 697 (1989).

[18]J. Darriet, C. J. P. Soethout, B. Chevalier, and J. Etourneau, Solid State Commun. **69**, 1093 (1989).

[19]W. Groen, D. M. Leeuw, and G. P. J. Geelen, Physica C **165**, 305 (1990).

[20]A. Maeda, M. Hase, I. Tsukada, K. Noda, S. Takebayashi, and K. Uchinokura, Phys. Rev. B **41**, 6418 (1990).

[21]J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezinge, T. C. Huang, and S. S. P. Parkin, Phys. Rev. Lett. **61**, 1127 (1988).

[22]Y. Tokura, J. B. Torrance, T. C. Huang, and A. I. Nazzal, Phys. Rev. B **38**, 7156 (1988).

[23]Y. Koike, Y. Iwabuchi, S. Hosoya, N. Kobayshi, and T. Fukase, Physica C **159**, 105 (1989).

[24]P. Bordet, J. J. Capponi, C. Chaillout, J. Chenavas, A. W. Hewat, E. A. Hewat, J. L. Hodeau, M. Marezio, J. L. Tholence, and D. Tranqui, Physica C **156**, 189 (1988).

[25]B. C. Sales and R. Viswanathan, J. Low Temp. Phys. **23**, 449 (1976).

[26]K. A. Gschneidner, Jr., *Rare Earth Alloys* (Van Nostrand, Princeton, 1961).

[27]W. Bauhofer, Hj. Mattausch, R. K. Kremer, P. Murugaraj, and A. Simon, Phys. Rev. B **39**, 7244 (1989).

[28]J. L. Tallon, Physica C **168**, 86 (1990).

[29]M. H. Whangbo and C. C. Torardi, Science **249**, 1143 (1990).

[30]For a review see, J. T. Markert, Y. Dalichaouch, and M. B. Maple, in *Physical Properties of High Temperature Superconductors I*, edited by D. M. Ginsberg (World Scientific, Singapore, 1989), p. 266.

[31]J. J. Neumeier, T. Bjornholm, M. B. Maple, and I. K. Schuller, Phys. Rev. Lett. **63**, 2516 (1989).

[32]C. L. Seaman, J. J. Neumeier, M. B. Maple, L. P. Le, G. M. Luke, B. J. Sternlieb, Y. J. Uemura, J. H. Brewer, R. Kadono, R. F. Kiefl, S. R. Krietzman, and T. M. Riseman, Phys. Rev. B **42**, 6801 (1990).

[33]G. Y. Guo and W. M. Temmerman, Phys. Rev. B **41**, 6372 (1990).

[34]F. W. Lytle, G. van der Laan, R. B. Greegor, E. M. Larson, C. E. Violet, and J. Wong, Phys. Rev. B **41**, 8955 (1990).